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NATURE OF THE GLASS IN PORTLAND CEMENT CLINKER

By Herbert Insley

ABSTRACT

New microscopical methods resulting in more accurate differentiation of the minor constituents of portland cement clinker are described which involve the etching of polished surfaces of the clinker grains by strong alkaline solutions. By the new technique it is possible to identify interstitial glass high in iron which heretofore has been confused in microscopical analysis with $4CaO.Al_2O_3.Fe_2O_3$. The results of microscopical analysis, using the new etching technique, are compared with results of an older microscopical method and with those of a heat-of-solution method.

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I. INTRODUCTION

In a recent paper [1][1] a method was outlined for determining quantitatively the constituents in portland cement clinker by the microscopical analysis of polished surfaces of clinker after etching with suitable reagents. The constituents $3CaO.SiO_2$, $2CaO.SiO_2$, "light interstitial" material, "crystalline dark interstitial" material, "glassy dark interstitial" material, free CaO, and free MgO were differentiated by using as etching reagents water followed by a 1 percent alcoholic solution of HNO_3. The quantitative analyses were made with a recording micrometer stage attached to the microscope. The volume proportions thus found were calculated to weight percentages by assigning density values to the constituents. Twenty-six samples of commercial portland cement clinker analyzed by the method just described were also analyzed chemically and the results calculated to compound composition by the Bogue method [2]. For 14 of these samples the glass content was determined by an independent method involving the determination of the heat of solution [3].

A comparison of the results of the different methods showed that the amount of glass found by the heat-of-solution method was greater in every case than was found by the microscopical method and that the amount of "light interstitial" material determined microscopically was greater than the $4CaO.Al_2O_3.Fe_2O_3$ calculated from chemical analyses for samples with Al_2O_3/Fe_2O_3 ratios less than 2.00. Indeed, for several samples the microscopically determined "light interstitial"

[1] Figures in brackets indicate the literature references at the end of this paper.

material equalled or exceeded the sum of the calculated $4CaO.Al_2O_3.Fe_2O_3$ and $3CaO.Al_2O_3$. The observation was made in the former paper that attempts to differentiate the "light interstitial" material into two phases (for instance, the compound $4CaO.Al_2O_3.Fe_2O_3$ and a highly refractive glass) by the use of etching reagents or illumination methods had thus far been unsuccessful.

Since the publication of that paper, the search for an explanation of the discrepancies mentioned has been renewed. The present paper is a record of some of the methods tried and a description of the method found successful, together with corrected results of the quantitative microscopical analysis, using the new method.

II. METHODS AND RESULTS

1. QUALITATIVE ANALYSES

As material for investigation three samples were selected from the 26 samples of commercial clinker previously studied. These samples, numbered originally 11, 12, and 16, showed the greatest differences between glass as determined microscopically and as determined by the heat-of-solution method. For the same samples microscopically determined, "light interstitial" material was also considerably greater than the calculated $4CaO.Al_2O_3.Fe_2O_3$. The pertinent data, in weight percentages, are given in table 1.

TABLE 1.—*Content of interstitial materials in clinker samples*

Sample No.[1]	Light interstitial		Glass	
	$4CaO.Al_2O_3.Fe_2O_3$ [2]	Microscopic	Microscopic	Lerch method [3]
	Percent	*Percent*	*Percent*	*Percent*
11	15	23	4	12
12	13	20	3	10
16	12	23	2	11

[1] From table 2 [1].
[2] Calculated by the Bogue method.
[3] The heat-of-solution method [3].

Specimens of all three clinker samples were first investigated by examining the powdered specimens in transmitted light with the petrographic microscope. The powders were immersed in a liquid of refractive index 1.74 so that all clinker constituents except $4CaO.Al_2O_3.Fe_2O_3$ and iron-bearing glass would have indices of refraction less than that of the immersion liquid. Using an arc lamp as light source and an oil-immersion objective, the grains with index higher than 1.74 were carefully tested for the presence or absence of material having double refraction. Practically all grains so examined contained prismatic birefringent crystals often pleochroic with a greenish-amber color and having indices of refraction markedly higher than that of the immersion medium. In some grains these crystals were intermingled, forming such a mat that no isotropic material could be seen, whereas in others what apparently was a greenish isotropic material formed a matrix for a few of the tiny crystals. The presence of an isotropic interstitial material with high index of refraction could not, however, be conclusively demonstrated by this method.

A study was then made of the effect of various etching reagents on polished surfaces examined in reflected light. Specimens of the same three clinker samples were used. A number of solutions in varying concentrations and for various etching periods failed to give any clear-cut differentiation of the light interstitial material.[3]

Neither oxalic acid nor hydrofluoric acid, recommended by Tavasci [4] to distinguisb "celite a" from "celite b," was found to be of help in this problem. Another reagent mentioned by Tavasci for etching $4CaO.Al_2O_3.Fe_2O_3$, a mixture of 4 parts by volume of 10 percent NaOH and 1 part of 10 percent Na_2HPO_4, when used under the specified conditions of 50° C for 1 minute, etched all the interstitial material indiscriminately. At room temperature, however, portions of the interstitial material were etched very slightly by this reagent, whereas other portions were etched more deeply. The more deeply etched areas included those etched by water and by the alcoholic solution of HNO_3 as well as much interstitial material left unetched by these reagents. Attention was, therefore, turned to strongly alkaline solutions. Both NaOH and KOH were satisfactory under proper conditions, but KOH produced stronger etching of the dark interstitial material and gave better contrast of the etched with the unetched material. A 10 percent aqueous solution in contact with the polished specimen for 15 seconds at 29° to 30° C gave the best results. The marked increase in the dark interstitial material shown by the KOH etch over that shown by the water and HNO_3 etches in clinkers with low Al_2O_3/Fe_2O_3 ratios can be seen by a comparison of figure 1 with figure 2. Much interstitial material apparently unetched in figure 1 is shown deeply etched in figure 2. In a quantitative microscopical analysis the material shown as unetched by water and HNO_3 in figure 1 would be included under light interstitial material, whereas much of the same area would be included in dark interstitial material as etched by KOH (fig. 2).

Figures 3 and 4 are of a polished area from another piece in the same clinker batch as represented in figures 1 and 2. The mottled effect seen in the dark interstitial area in figure 2, and more noticeably in figure 4, indicates that such areas are not composed of a single homogeneous phase. Examination of similar areas in polished thin sections with transmitted light shows the presence of an isotropic material with green color and a high refractive index. Such optical properties are characteristic of a glass containing a considerable amount of iron. This material is the matrix for tiny, amber, needle-like crystals, with high index of refraction and moderately high birefringence, having the appearance of $4CaO.Al_2O_3.Fe_2O_3$. Areas like the unetched interstitial areas in figures 2 and 4 contain much larger crystals of $4CaO.Al_2O_3.Fe_2O_3$ without accompanying glass. Such areas were found very close to the surface of small clinker grains less than 6 mm in diameter. It is impossible to say whether or not a concentration of certain constituents near the surface caused by a volatilization of alkalies or by a migration of iron oxide was responsible for this condition. Larger clinker grains from the same batch contain interstitial material like that shown in figures 5 and 6, the glass apparently forming a matrix for prismatic crystals of $4CaO.Al_2O_3.Fe_2O_3$. Figures 7 and 8 illustrate the relations of interstitial material in clinker

[3] It was observed incidentally that a 5-percent solution of NH_4Cl in water, when applied for about 3 seconds at room temperature, brought out more clearly than other reagents the internal structure of crystals of $2CaO.SiO_2$ and $3CaO.SiO_2$, especially zonal growths and twinning bands.

sample 11 with an Al_2O_3/Fe_2O_3 ratio of 1.12. In this clinker sample the ratio of $4CaO.Al_2O_3.Fe_2O_3$ to glass is obviously greater than in sample 16, probably because of the lower Al_2O_3/Fe_2O_3 ratio in the former.

The nature and etching behavior of the interstitial constituents are confirmed by a study of polished sections of mixtures composed only of CaO, Al_2O_3, Fe_2O_3, and SiO_2, heated and quenched under known conditions. Samples of one such mixture having the composition CaO 63.7 percent, SiO_2 24.5 percent, Al_2O_3 5.9 percent, and Fe_2O_3 5.9 percent, with the calculated compound composition (by the Bogue method) of $3CaO.SiO_2$ 25 percent, $2CaO.SiO_2$ 51 percent, $3CaO.Al_2O_3$ 6 percent, and $4CaO.Al_2O_3.Fe_2O_3$ 18 percent, were quenched from the temperatures 1,500°, 1,345°, 1,340° and 1,330° C. In spite of care, preparations entirely free of quench growths were not obtained. A favorable area in the 1,500° C preparation showing few quench growths is seen in figure 9 after etching with H_2O for 3 seconds followed by a 0.25 percent alcoholic solution of HNO_3 for 3 seconds. The interstitial material appears highly reflecting and homogeneous. After treatment with 10 percent KOH solution for 15 seconds at 30° C, the interstitial material is etched and darkened (fig. 10) without showing evidence of differentiation. The 1,345° C preparation should, according to the equilibrium diagram of this system [5], contain crystals of $4CaO.Al_2O_3.Fe_2O_3$ and glass in the interstitial material. As seen in figure 11, the interstitial material shows a slight differentiation into light and dark areas after etching with water and nitric acid and a much more pronounced differentiation after etching with the 10 percent KOH solution (fig. 12). In the 1,340° C preparation differentiation with the water and nitric acid etches (figs. 13 and 14) is still more pronounced than in the 1,345° C preparation (fig. 11) and the quantity of light interstitial material ($4CaO.Al_2O_3.Fe_2O_3$) has increased at the expense of the dark interstitial material (glass). In the preparation which was quenched at 1,330° C, a temperature below the invariant temperature (1,338° C) in this portion of the system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ [5], the interstitial constituents, crystalline $4CaO.Al_2O_3.Fe_2O_3$ and crystalline $3CaO.Al_2O_3$, are readily differentiated with H_2O and HNO_3 (fig. 15). Further treatment with KOH etches the $3CaO.Al_2O_3$ more deeply, but does not increase the apparent amount of the etched interstitial material (fig. 16).

Parker and Nurse [6] have deduced from indirect evidence that the nitric acid solution etches glasses in portland cement clinker relatively low in iron but not those high in iron. The preceding group of experiments confirms this deduction, because the amount of Fe_2O_3 in the glass is decreased as the temperature of heat treatment is lowered.

It is not safe, however, to draw conclusions concerning the iron content of glasses in commercial clinkers from such laboratory experiments. Figures 2 and 6 are photomicrographs of different clinker pieces from the same commercial sample. It is apparent that the structure of the interstitial matter and the relative amounts of glass present are quite different and, therefore, it is reasonable to assume that the iron content of the glass in the two pieces is different. Such differences in individual pieces may be caused not only by variations in the composition of the batch but by the rates at which the clinker pebbles pass from the hot zone of the rotary kiln to the exit end.

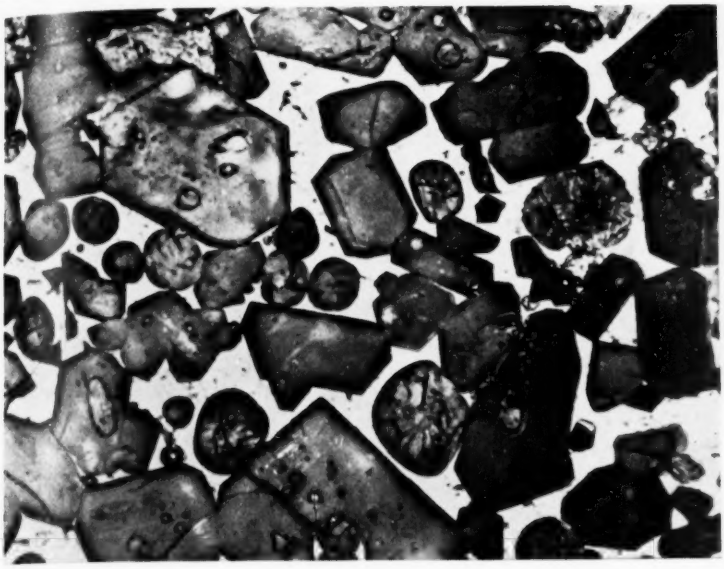

FIGURE 1.—*Clinker sample 16* ($Al_2O_3/Fe_2O_3=1.34$) *after etching with water for 2 seconds followed by a 1-percent alcoholic solution of* HNO_3 *for 2 seconds.*

Lack of differentiation of interstitial material is shown. Reflected light. Magnification, ×500.

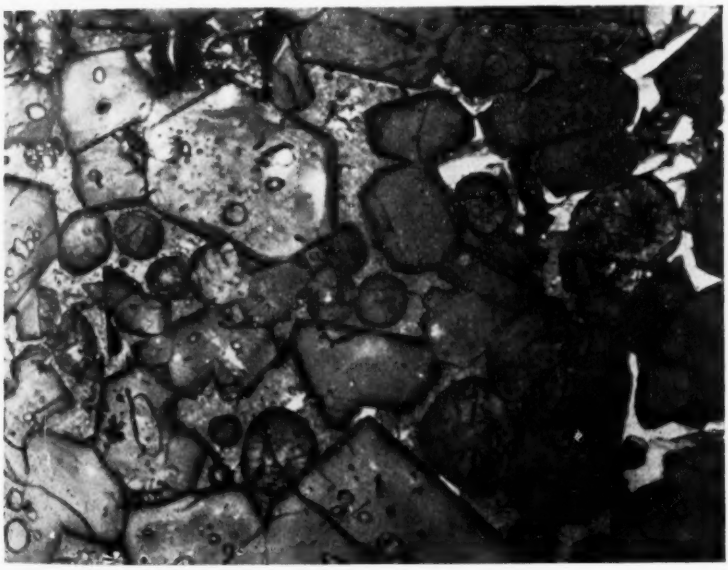

FIGURE 2.—*Same field as figure 1 after the same etching treatment and an additional etching with 10 percent* KOH *for 15 seconds at 29° C.*

Marked differentiation of interstitial material is shown. Reflected light. Magnification, ×500.

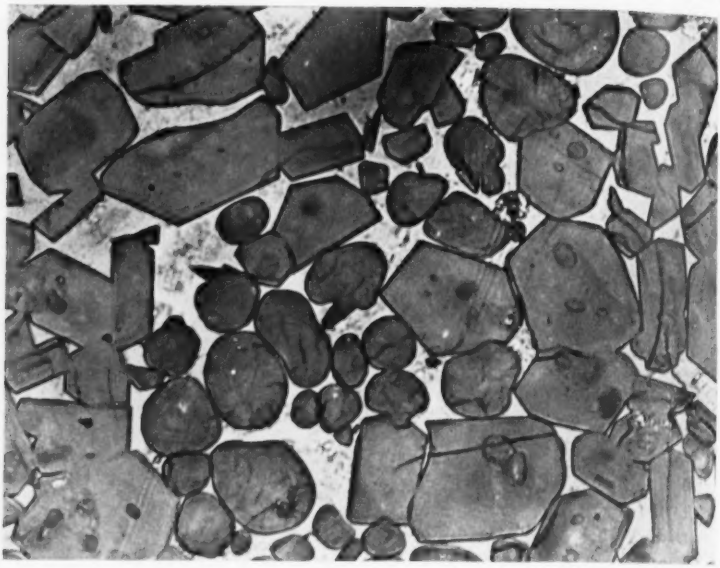

FIGURE 3.—*Clinker sample 16 (a different field from fig. 1) after etching with water and a 1-percent alcoholic solution of* HNO_3.

Reflected light. Magnification, ×500.

FIGURE 4.—*Same field as figure 3 after the same etching treatment and an additional etching with 10 percent* KOH.

Showing marked differentiation of interstitial material with intimate mixture of glass and small C_4AF crystals in deeply etched interstitial areas. Magnification, ×500.

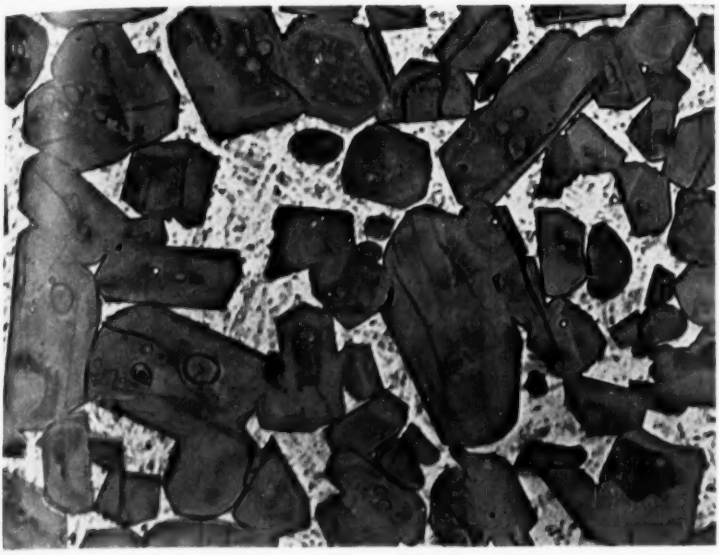

FIGURE 5.—*Clinker sample 16 (a different field from figures 1 and 3) after etching with water and a 1-percent alcoholic solution of* HNO_3.

Slight differentiation of interstitial material is shown. Reflected light. Magnification, ×500.

FIGURE 6.—*Same field as figure 5 after the same etching treatment and an additional etching with 10 percent* KOH.

Marked differentiation of interstitial material into prismatic C_4AF crystals and matrix glass is shown. Magnification, ×500.

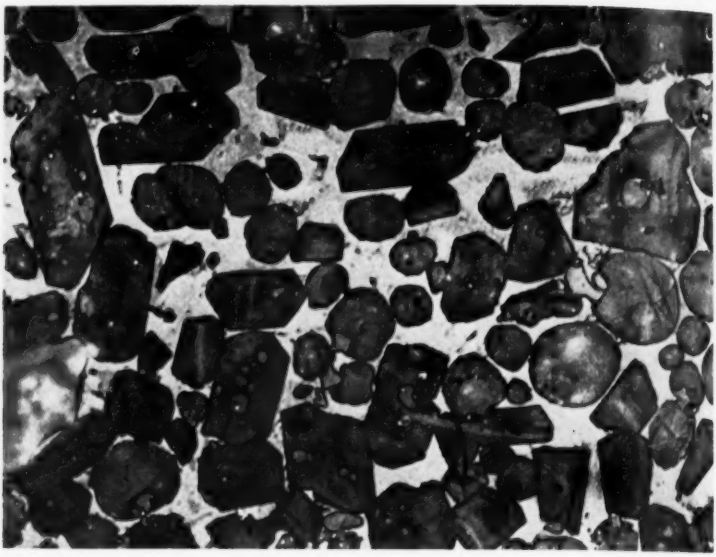

FIGURE 7.—*Clinker sample 11* ($Al_2O_3 = 1.1\%$) *after etching with water followed by 1-percent alcoholic solution of* HNO_3.

Very slight differentiation of interstitial material is shown. Reflected light. Magnification, ×500.

FIGURE 8.—*Same field as figure 7 after the same etching treatment and an additional etching treatment with 10 percent* KOH.

Relatively larger amounts of C_4AF and smaller amounts of glass than in clinker sample 16 are shown. Reflected light. Magnification, ×500.

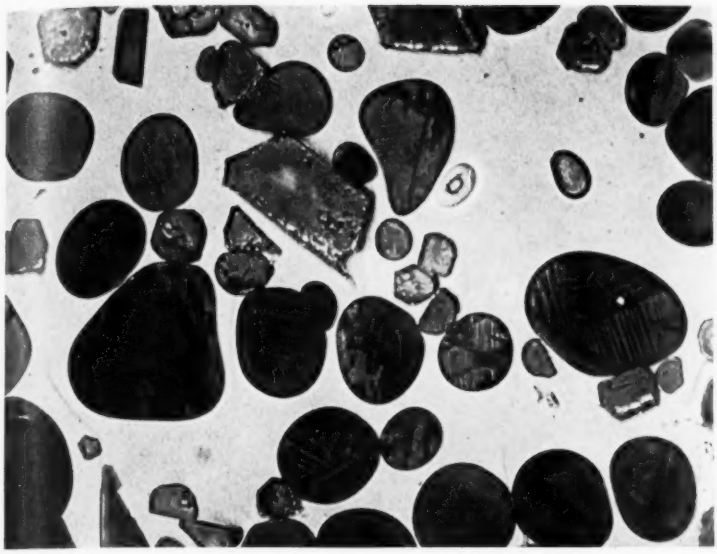

FIGURE 9.— *Laboratory-prepared low-heat clinker quenched after heating at 1,500° C.*

Etched with water for 2 seconds followed by 1-percent alcoholic solution of HNO_3 for 2 seconds. Highly reflecting, undifferentiated character of interstitial material is shown. Reflected light. Magnification, ×730.

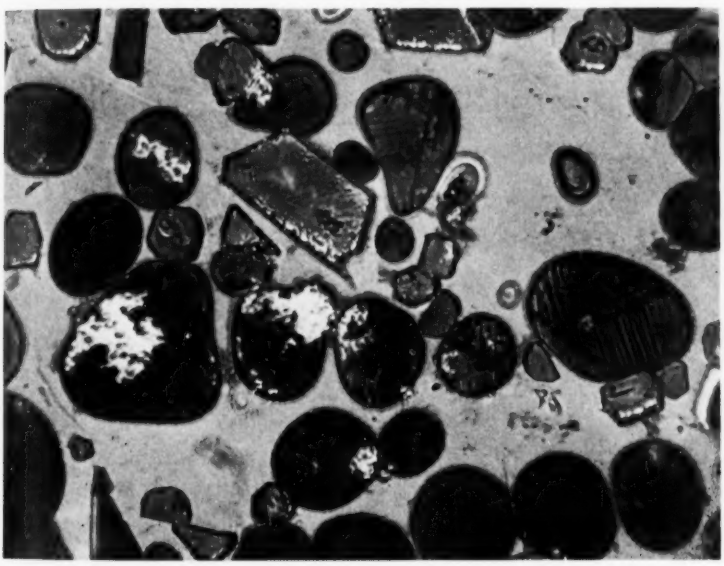

FIGURE 10.— *Same field as figure 9 after the same etching treatment and an additional etching with 10 percent* KOH *for 15 seconds at 29° C.*

The appearance of quench-growth halos around C_3S grains and a general decrease in reflectivity of the interstitial material are shown. Reflected light. Magnification ×730.

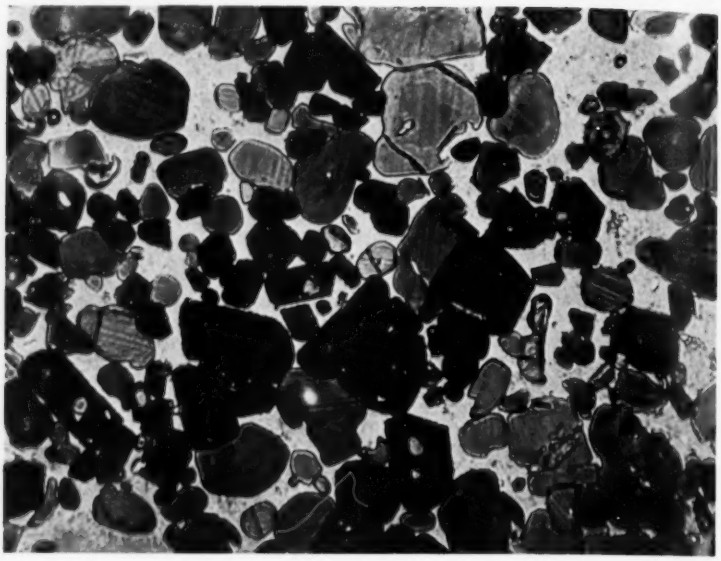

FIGURE 11.—*Laboratory-prepared low-heat clinker quenched after heating at 1,345° C.*

Etched with water and 1-percent alcoholic solution of HNO_3. Very slight differentiation of interstitial material is shown. Reflected light. Magnification, ×730.

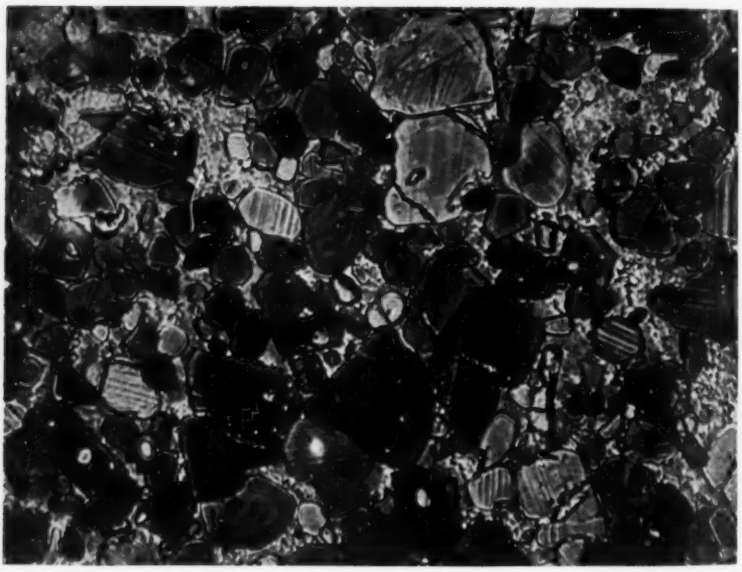

FIGURE 12.—*Same field as figure 11 after the same etching treatment and an additional etching with 10 percent* KOH.

The mottled character and the marked differentiation of the interstitial material are shown. Reflected light. Magnification, ×730.

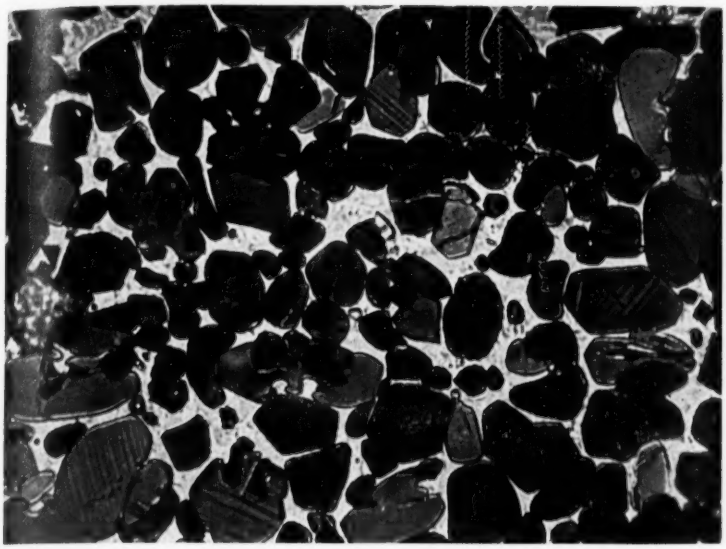

FIGURE 13.—*Laboratory-prepared low-heat clinker quenched after heating at 1,340° C.*

Etched with water and 1-percent alcoholic solution of HNO_3. Shows greater differentiation of interstitial material than figure 11. Reflected light. Magnification, ×730.

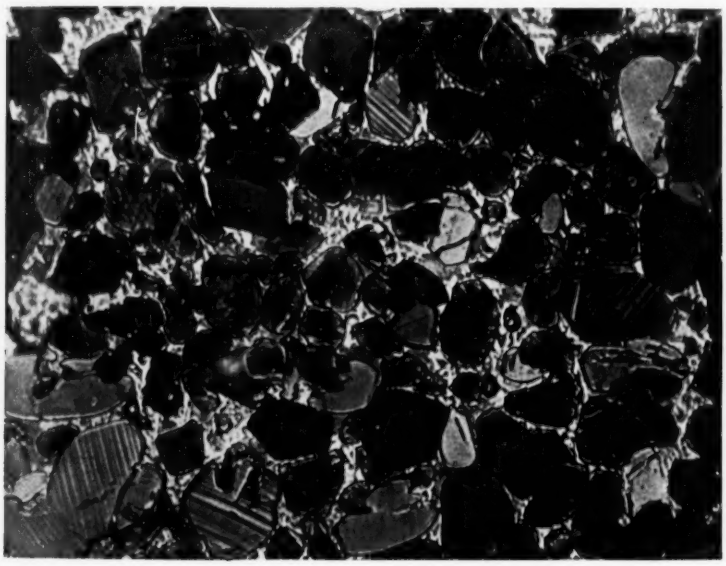

FIGURE 14.—*Same field as figure 13 after the same etching treatment and an additional etching with 10 percent* KOH.

The phase separation in the interstitial material is shown. Reflected light. Magnification, ×730.

FIGURE 15.—*Laboratory-prepared low-heat clinker quenched after cooling from 1,350 to 1,330° C.*

Marked distinction between interstitial phases (C_4AF and C_3A) is shown. Magnification, ×730.

FIGURE 16.—*Same field as figure 15 after the same etching treatment and an additional etching with 10 percent* KOH.

No increase in distinction of interstitial phases over that in figure 15 is shown. Reflected light. Magnification, ×730.

2. QUANTITATIVE ANALYSES

The amount of glass made visible by the KOH solution was so much greater than that revealed by the HNO_3 solution in certain clinker samples that it was decided to reanalyze quantitatively for $4CaO.Al_2O_3.Fe_2O_3$ and glass all those samples whose analyses were reported in the previous paper [1]. The methods of mounting the clinker specimens and of measuring the phases were the same as described in that paper. The polished surfaces of the clinker fragments were etched first with distilled water for 3 seconds, then with an alcoholic solution of 0.25 percent HNO_3 for 3 seconds to provide satisfactory distinction between the silicates and $4CaO.Al_2O_3.Fe_2O_3$, and finally with a 10 percent aqueous solution of KOH at 29°C for 15 seconds.

TABLE 2.—*Compositions of commercial clinker samples as determined by different methods*

Clinker [1]	Free CaO plus free MgO [2] (microscopic)	$2CaO.SiO_2$ plus $3CaO.SiO_2$ (microscopic)	Light interstitial			Crystalline dark interstitial [2]	Glass			Al_2O_3/Fe_2O_3 ratio
			Calculated $4CaO.Al_2O_3.Fe_2O_3$ [3]	First microscopic [2]	Second microscopic		First microscopic [2]	Second microscopic	Lerch method	
	Volume (%)	*Volume* (%)	*Volume* (%)	*Volume* (%)	*Volume* (%)	*Volume* (%)	*Volume* (%)	*Volume* (%)	*Weight* (%)	*Volume* (%)
1	3	79	13	16	13	1	1	4	3	0.86
2	0	76	16	22	15	0	2	9	5	.89
3	0	75	16	18	17	4	3	4	.....	.91
4	0	68	19	27	24	1	4	7	.....	.91
5	3	72	16	21	17	2	2	6	5	.92
6	2	78	14	17	14	1	2	5	7	.92
7	4	76	13	17	11	0	3	9	.....	1.01
8	2	79	10	16	10	1	2	8	.....	1.07
9	3	74	14	19	17	1	3	5	6	1.12
10	2	76	13	19	14	1	2	7	3	1.12
11	1	74	13	20	15	1	4	9	12	1.12
12	2	77	12	18	14	0	3	7	10	1.12
13	0	81	12	16	12	2	1	5	.....	1.22
14	1	74	14	21	21	1	3	3	.....	1.23
15	1	72	13	22	19	1	4	7	5	1.25
16	0	77	11	20	12	1	2	10	11	1.34
17	0	85	6	10	7	3	2	5	8	1.73
18	1	70	10	19	13	6	4	10	5	1.78
19	1	72	9	9	9	9	9	9	13	2.07
20	0	75	8	9	9	13	3	3	.....	2.11
21	1	71	8	6	8	12	10	8	.....	2.53
22	3	78	5	5	5	6	8	8	.....	2.64
23	2	69	8	9	9	14	6	6	.....	2.68
24	5	73	5	6	6	6	10	10	.....	2.78
25	3	75	6	4	6	8	10	8	13	2.89
26	0	76	5	5	6	15	4	3	.....	3.73

[1] Same designation as in Research Paper 1135, table 2.
[2] Determined by method described in Research Paper 1135.
[3] Calculated by the Bogue method from the chemical composition.

The results of this analysis are given in table 2 under the headings, "Light interstitial—2d microscopic" and "Glass—2d microscopic." For comparison, these columns are set adjacent to columns with the subheadings "1st microscopic," under which are given the results for light interstitial material and glass as reported in Research Paper 1135. The table also gives the microscopically determined free CaO plus free MgO, $2CaO.SiO_2$ plus $3CaO.SiO_2$, the crystalline dark interstitial

material, $4CaO.Al_2O_3.Fe_2O_3$ as calculated by the Bogue method, glass by the heat-of-solution method (designated the Lerch method), and the Al_2O_3/Fe_2O_3 ratio. Unlike table 2 of Research Paper 1135, all percentage values, except those for the Lerch method, are given here on the volume basis because no satisfactory density values can be assigned to the glasses to convert volume percentages as determined microscopically to weight percentages.

It is evident from an inspection of the table that the values for glass are higher and those for $4CaO.Al_2O_3.Fe_2O_3$ are lower by the second microscopical method (using the KOH etch) than by the first microscopical method (using the HNO_3 etch) for all samples with Al_2O_3/Fe_2O_3 ratios less than 2.00. For ratios greater than 2.00, the values by the two methods are approximately the same. Consequently, the quantitative analyses provide additional evidence that the nitric acid solution etches glasses low in iron but fails to etch those high in iron, whereas the potassium hydroxide solution etches both.

Comparing the results for glass by the first and second microscopical methods with those obtained by heat-of-solution shows closer agreement between the second microscopical and heat-of-solution methods. Nevertheless, there are still discrepancies, notably for samples 2, 10, and 18. In part these discrepancies are the results of errors in the microscopical determination as, for example, the inability to distinguish and to measure accurately the amounts of $4CaO.Al_2O_3.Fe_2O_3$ and glass in areas where very fine particles of these two constituents are intimately mixed, and in part these discrepancies are the results of acknowledged errors [3] in the heat-of-solution method.

III. SUMMARY

A method of etching the polished surfaces of portland cement clinkers with KOH solution is described. This method permits the detection of glass containing considerable iron which has been hitherto overlooked in microscopical examination. The results of quantitative microscopical analysis using this technique are reported and compared with the results obtained by an older method.

The later results are practically identical with the earlier results for clinkers with Al_2O_3/Fe_2O_3 ratios greater than 2.00, but for those with ratios less than 2.00, the later results give more glass and less $4CaO.Al_2O_3.Fe_2O_3$ than the earlier results. The quantitative results for glass by the later microscopical technique are more nearly in agreement with the results by an independent method involving the determination of heat-of-solution.

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IMPROVEMENTS IN THE PREPARATION OF *d*-GALACTURONIC ACID

By William Ward Pigman

ABSTRACT

Many plant materials, particularly the pectins, consist to a considerable extent of polymers of *d*-galacturonic acid. Of the methods available for the preparation of *d*-galacturonic acid, enzymatic methods are considered preferable, since the acid is rapidly decomposed by hot mineral acids. The use of enzymes for this purpose has been previously described, but the methods either result in poor yields or employ materials or enzymes not conveniently available. The present paper describes an improved method which results in yields of *d*-galacturonic acid of more than 67 percent of the theoretical values and which makes use of commercially available materials.

The uronic acids are important and widely distributed constituents of natural products. Pectin, an important carbohydrate, has been shown by Ehrlich and his collaborators[1] to be primarily a polymer of galacturonic acid. Another well-known uronic acid is glucuronic acid, which functions in animals as a detoxifying agent and is usually made by feeding animals substances such as benzoic acid. The glucuronide formed is recovered from the urine of the animal and converted to the acid. These acids have the formula CHO-(CHOH)$_4$-COOH (written as the free aldehyde form). They have the properties of sugars and acids and are capable of forming a great number of derivatives and of undergoing many isomeric transformations. The older methods of preparation of the uronic acids have not been very satisfactory, and as a result their price has been very high.

Since the uronic acids are relatively easily decomposed by acids,[2] biological methods for their preparation would seem to be preferable to methods using acid hydrolysis.[3] Ehrlich[4] has reported an enzymatic method which gives high yields, but which requires materials not easily obtained in this country. Mottern and Cole,[5] however, have reported a method which uses commercially available citrus pectic acid (citrus polygalacturonide) and pectinase and thus have provided a very convenient method for the preparation of galacturonic acid. The method consists in its essentials in hydrolyzing a pectin derivative with a commercial pectinase preparation and then extracting the *d*-galacturonic acid with ethyl alcohol. The maximum yield reported for the Mottern and Cole method has been 37 percent of the

[1] F. Ehrlich, Z. angew. Chem. **40**, 1305 (1927).
[2] R. L. Whistler, A. Martin, and M. Harris, J. Research NBS **24**, 13 (1940) RP1268.
[3] F. Ehrlich and F. Schubert, Ber. deut. chem. Ges. **62**, 1974 (1929).
S. Morell, L. Bauer, and K. P. Link, J. Biol. Chem. **105**, 15 (1934).
[4] F. Ehrlich, Abderhalden's Handbuch der biologischen Arbeitsmethoden, Abt. 1, Teil 11, 1617 (1936); F. Ehrlich, Enzymologia **3**, 185 (1937).
[5] H. H. Mottern and H. L. Cole, J. Am. Chem. Soc. **61**, 2701 (1939).

theoretical,[6] while Ehrlich (see footnote 4) has obtained yields of 85 percent.

It has now been found that by the use of methyl alcohol as a solvent and by a few minor changes in the Mottern and Cole procedure, it is possible to increase the average yield to more than 70 percent of the weight of the citrus polygalacturonide used as the starting material. Assuming the galacturonic content of the citrus polygalacturonide to be 95 percent (see footnote 7), this corresponds to a theoretical yield of 67 percent. Since the materials used are all commercial products of comparatively low cost, and since the procedure is simple, *d*-galacturonic acid can be produced at a cost not greatly exceeding some of the fairly common sugars, such as *d*-galactose.

The methyl alcohol has the advantage that it dissolves the galacturonic acid much more readily than ethyl alcohol and also that the extent of conversion to more soluble isomers is lessened. In the original method, considerable galacturonic acid was left in the insoluble residue. This was proved, since such residues were found to yield considerable quantities of galacturonic acid when they were extracted with methyl alcohol. This probably also explains the increase in yield reported by Manville, Reithel, and Yamada (see footnote 6), who gave the residue an acid treatment and extraction. The acid treatment has now been found to be unnecessary and probably detrimental, since the mother liquors are decomposed by the acid.

Procedure.—Two solutions were prepared as follows and combined after the hydrolytic period. To 2,600 ml of water stirred well at 40° C, there was added 260 g of citrus polygalacturonide [7] and then 385 ml of 3 *N* sodium hydroxide. To this viscous solution, which has a pH of about 3.7 at 37° C, there was added 20 g of pectinase,[8] and the solution was kept at 38° C for 10 to 14 days. Mold growth was prevented by covering the surface of the solution with a thin layer of toluene.

After the period of hydrolysis, the two solutions were combined and an amount of sulfuric acid equivalent to the sodium hydroxide originally used was added. The solution was filtered with the help of diatomaceous earth and the residue washed with 700 ml of water. The filtrate was treated with 170 g of activated charcoal (Norite) and filtered after 24 hours. The thick sirup obtained by evaporating the filtrate weighed 737 g and was treated with 2 liters of boiling methyl alcohol. The solution was heated to the boiling point and then separated from the crystalline salts (principally sodium sulfate) by filtration. The salts were then given a second extraction by boiling them for 5 minutes with a 1-liter portion of methyl alcohol. When the extractions were carried out carefully, two were found to be sufficient.

The combined extracts were evaporated under reduced pressure to a volume of about 900 ml, and the addition of a small amount of ethyl alcohol sufficed to saturate the solution. The solution, after seeding, was kept for 24 to 48 hours in a refrigerator at about 5°C, and during this time it was stirred frequently. The crystals, after

[6] I. Manville, F. Reithel, and P. Yamada, J. Am. Chem. Soc. **61,** 2973 (1939).

[7] K. P. Link and R. Neddon, J. Biol. Chem. **94,** 307 (1931–32). The product was supplied by the California Fruit Growers Exchange, Ontario, Calif., under the name of citrus pectic acid.

[8] The material used was Röhm and Haas Pectinol 46AP, standardized with diatomaceous earth (100D). It is not known with certainty, but it is believed that this enzyme material is the same as that reported by Z. I. Kertesz, J. Am. Chem. Soc. **61,** 2544 (1939), as being produced by the precipitation with ethyl alcohol of a water extract from *Aspergillus sp.* grown on a special medium.

separation by filtration, washing with methyl alcohol containing 10 to 20 percent of water, and thorough drying at room temperature, weighed 255 g. The mother liquors were evaporated to a thin sirup, methyl alcohol was added until amorphous material began to precipitate and the solution was allowed to crystallize in the refrigerator for several days. The crystals, washed and dried as before, weighed 71 g. The mother liquors were then worked up by repeating the following procedure until practically all of the methyl alcohol-soluble material had been obtained in crystalline condition. The mother liquors were evaporated in vacuo to a thick sirup,[9] which was extracted by boiling several times with methyl alcohol. The solution was separated from the insoluble material [10] by decantation and concentrated to a thin sirup, which was allowed to crystallize for several days at a low temperature. Sometimes the addition of methyl or absolute ethyl alcohol is advantageous. The crystals were washed with 80- to 90-percent methyl alcohol. From the mother liquors, 59 g more of fairly white material was obtained.

The first crops weighed 254 g, were white in color, and had a melting point of 109° to 112°C. The equilibrium rotation was $[\alpha]_D^{20}=+51.5$ (c, 4). The almost colorless materials of slightly lower purity weighed 130 g, melted at 105° to 107° C, and had an equilibrium rotation of $[\alpha]_D^{20}=+51.5$ (c, 5.2). The pure galacturonic acid monohydrate, called the alpha isomer by Ehrlich and Schubert (see footnote 3), melts at 156° to 159° C after sintering at 110° C, and its equilibrium rotation (see footnote 3) is $[\alpha]_D^{20}=+50.9$. The total yield is then 385 g, or 74 percent, of the weight (520 g) of the starting material.

WASHINGTON, July 16, 1940.

[9] The temperature of the outside bath during the final stages of the evaporation should be kept as low as possible.

[10] This amorphous organic material is quite acid and presumably is an isomer of galacturonic acid or is a condensation product of this acid possibly analogous in structure or in origin to the Schardinger dextrins, which are obtained in a similar way. Additional quantities of this material have also been obtained by extracting the sodium sulfate residue with boiling 85-percent methyl alcohol.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1326

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PECTIC SUBSTANCE OF COTTON FIBERS IN RELATION TO GROWTH

By Roy L. Whistler,[1] Albert R. Martin,[1] and Carl M. Conrad [2]

ABSTRACT

The content of pectic substance in cotton fibers at various stages of growth was determined. The results suggest three distinct stages of development of the fiber. The first extends to about the 18th day and is characterized by a gradual decrease in the content of pectic substance. The second extends from the 18th to about the 35th day, during which time there occurs a rapid decrease in the content of pectic substance. In the final stage, which extends from about the 35th day to maturity, there is only a slight decrease in the content of pectic substance. These three stages of development are in good agreement with those deduced by other investigators from different types of data.

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I. INTRODUCTION

It has been suggested [1] [3] that the pectic substance of cotton fibers is largely confined to the primary cell wall. Thus it would be expected that very young cotton fibers would contain a high percentage of pectic substance and that the percentage would decrease as fiber development progresses and would reach its lowest value at the time of fiber maturity. It was the purpose of the present investigation to examine this concept quantitatively by following the changes in percentage of pectic substance during the course of the development of cotton fibers.

II. MATERIALS AND METHODS

The cotton fibers used in these experiments were collected during the summers of 1937 and 1939, from plants growing in the experiment station fields of the United States Department of Agriculture at Raleigh, N. C. The cotton was of the Mexican Big Boll variety of *Gossypium hirsutum*. The age of the fiber as collected in the field was determined by tagging the flowers on the day of blooming and

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Senior Cotton Technologist, Agricultural Marketing Service, United States Department of Agriculture.
[3] Figures in brackets indicate the literature references at the end of this paper.

then collecting the bolls at definite intervals. As soon as the bolls were picked, they were opened and the cotton fibers removed. The fibers which were to be used for the determination of uronic acids were quickly dried in a stream of warm air. Those used for the determination of pectic substance by the calcium pectate method were not dried but were quickly removed from the bolls at the time of picking and preserved in 80-percent ethanol.

Uronic acid determinations were made according to the procedure developed by Whistler, Martin, and Harris [2], and the results expressed as percentage of uronic acid–carbon dioxide on the basis of dry weight of the fibers, or as percentage of pectic substance. Conversion of uronic acid–carbon dioxide to pectic substance was accomplished by multiplying the percentage of carbon dioxide by the factor 4.8 [2]. The size of the samples taken for analysis varied from 2 to 10 g, depending upon the uronic acid content.

In addition to the determination of pectic substance by uronic acid analysis applied directly to the fibers, the 1937 series of fibers were analyzed for pectic substance by means of the calcium pectate method according to the following procedure. The sample (preserved in ethanol) was extracted 4 hours with 90-percent ethanol in a Soxhlet apparatus. The fibers, after drying in a vacuum oven at 60° C, were subjected to a 30-minute extraction with 100 ml of a boiling 0.5-percent solution of ammonium citrate, followed by three successive 30-minute extractions with fresh 100-ml portions of boiling 0.01 *N* hydrochloric acid. The entire cycle of four extractions was then repeated and the filtrates and washings were combined.[4]

The combined extracts were cooled, neutralized with sodium hydroxide solution, and the pectic substance was determined in an aliquot according to the procedure of Carre and Haynes [5]. The final calcium pectate precipitate was corrected for impurities by the method of Appleman and Conrad [6].

III. EXPERIMENTAL RESULTS AND DISCUSSION

The pectic substance content in cotton fibers at various stages of growth is shown in table 1 and figure 1. It is seen that the percentage of pectic substance as determined by the calcium pectate method is consistently lower than that found by the direct method of uronic acid analysis. However, since methods of isolation in general give somewhat low results, this difference is not unexpected.

An examination of the curves in figure 1 reveals that they are composed of three major segments; the first, extending to about the 18th day, indicates a gradual decrease in the percentage of pectic substance with age of the fiber; the second, extending from about the 18th to the 35th day, indicates a rapid decline in the percentage of pectic substance; the third, extending from about the 35th day to the time of maturity, indicates only a slight decrease in the percentage of pectic substance with age of the fiber. It seems probable that each of these periods may be related to particular phases of growth in the development of the cotton fiber. For example, if it is assumed that the pectic substance is largely confined to the primary cell wall, no large change in the percentage of the pectic substance should occur

[4] The frequent change of solvent and the low concentration of hydrochloric acid were employed [3, 4] to minimize destruction of the pectic substance.

during the period of primary wall formation. However, as nonpectic material, for example cellulose, is deposited in the fiber, the percentage of pectic substance should decrease in approximate inverse proportion with the amount of deposited nonpectic substance.

TABLE 1.—*Calcium pectate and pectic substance content of cotton fibers at various stages of growth*

Age of fiber	Calcium pectate	1937 series		1939 series	
		Uronic acid–carbon dioxide	Pectic substance content (calc.)	Uronic acid–carbon dioxide	Pectic substance content (calc.)
Days	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
10	4.39	1.24	5.95		
11	4.02				
12	4.05				
14	3.95				
16	3.24				
17	3.24	1.16	5.57		
18	3.21	1.13	5.43		
19	3.58	1.01	4.85		
20	3.44				
21	3.12				
22				1.04	4.99
23	2.39	.73	3.50		
24				.79	3.79
25	1.85	.68	3.22	.60	2.88
26				.47	2.26
28					
30	1.29	.39	1.87	.35	1.68
32				.31	1.49
34				.24	1.15
35	.83	.30	1.44		
36				.23	1.10
39				.24	1.15
40	.62	.19	.91		
42				.18	.86
45	.79	.20	.96	.21	1.00
48					
50	.67	.22	1.06		
51				.22	1.05
54				.21	1.00
OB		.17	.82	.19	.91

It has long been recognized that the first phase in the growth of the cotton fiber consists in the development and elongation of the primary cell wall. The time required for the completion of this phase, as measured by Anderson and Kerr [1] for cotton fibers of the Mexican Big Boll variety, is about 20 days. This is very near the age at which the curves in figure 1 undergo a sudden and rapid decline. Thus the present data suggest that no major changes in the composition of the fiber occur during this phase of development.

With the completion of the development of the primary cell wall, the formation of the secondary wall is initiated and a rapid deposition of cellulose commences. This should result in lowering the percentage of pectic substance in the fiber, especially if no appreciable amounts of pectic substance are laid down with the cellulose. The second segment of the curve confirms such an interpretation and further indicates the rate at which the development of the secondary wall proceeds. This interpretation is also in accord with the work of Berkley [7], in which it was shown that in cotton fibers similar to those used in this work, the secondary cell wall underwent a rapid thickening between the 18th and 35th days of growth. An examina-

tion of the change in the percentage of cellulose with the age of the fiber further substantiates these views.[5]

From about the 35th day until the boll opened, the content of pectic substance underwent little change, as indicated by the third segment of the curve. This is in agreement with the findings of Berkley [7], who also showed that no significant change in the ratio of thin- to thick-walled fibers occurred during this period—a fact which indicates that no appreciable change in wall thickness is occurring.

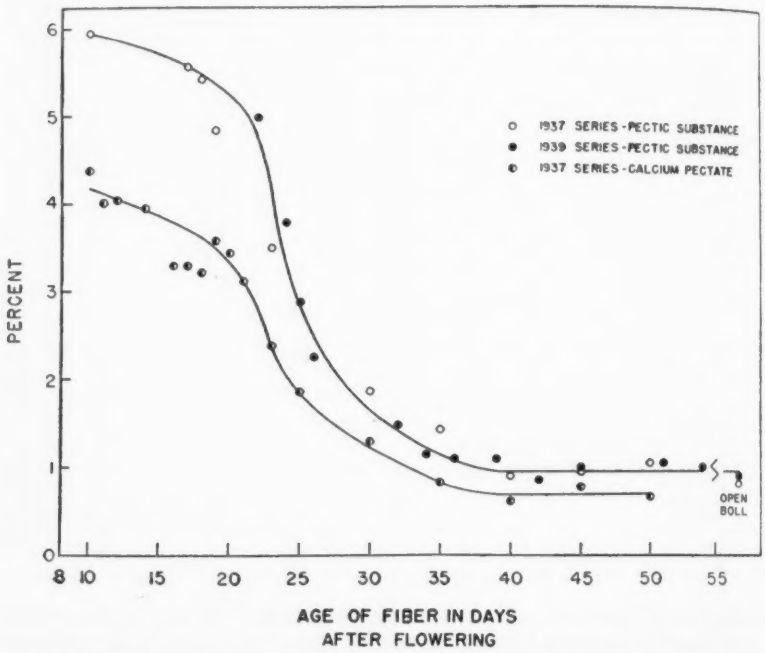

FIGURE 1. *The content of pectic substance of cotton fibers at various stages of growth.*

The upper curve was obtained from uronic acid analysis; the lower curve by isolation of the pectic substance as its calcium salt.

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[5] Carre, M. H., and Haynes, D., Biochem. J. **16**, 60 (1922).
[6] Appleman, C. O., and Conrad, C. M., Bul. 291 Univ. of Md. Expt. Sta. (1937).
[7] Berkley, E. E., Textile Research **9**, 355 (1939).

WASHINGTON, May 29, 1940.

[5] This report is in preparation for publication.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1327

Part of Journal of Research of the National Bureau of Standards, Volume 25, September 1940

PERMEABILITY OF ELASTIC POLYMERS TO HYDROGEN

By Theron P. Sager

ABSTRACT

The permeabilities to hydrogen of natural rubber, Perbunan, Neoprene *G*, Vistanex, Thiokol *Dx*, and Pliofilm diminished in the order of mention. The increase in rate of permeation with increasing temperature was exponential in all cases. Values for the activation energies of permeability for hydrogen were found to be 6,800 cal/mole for natural rubber and 8,400 to 9,500 cal/mole for the synthetic materials. The greater magnitude of the energy requirements of the latter indicates that their lower permeability may be attributed to differences in their molecular structure.

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I. INTRODUCTION

Natural rubber has been the material generally employed as the gas-retaining membrane in various inflated structures. This is because of its unique combination of high tensile strength and almost completely reversible extensibility. Its inherent limitations are low gas impedance and the lack of resistance to deterioration. There are relatively few materials which can be used for this purpose. A majority of the film-forming substances—cellulose derivatives, drying oils, resins—which are employed in varied applications in our economy, fail in one respect or another to meet the peculiar requirements. Within recent years however a number of synthetic materials have become available which are characterized by high elasticity and are also less permeable than rubber to gases. The values reported here result from a continuation of the study of the permeability of these materials for the Bureau of Aeronautics of the United States Navy Department.

II. MATERIALS AND METHOD

The materials which were examined included natural rubber; Perbunan, a co-polymer of butadiene and acrylonitrile; Neoprene *G*, one of the types of polymerized chloroprene; Thiokol *Dx*, a product resulting from the condensation of halogenated olefins and sodium polysulphide; Vistanex, a polymer composed of isobutene units; and Pliofilm, composed of rubber hydrochloride. Pliofilm is not a rubber-like material, although it is somewhat extensible and exhibits elasticity at elevated temperatures. This material was examined in the form

in which it was received. Films, ranging in thickness from 0.025 to 0.06 cm, were prepared from the other materials. Those materials which attain their most desirable physical properties as the result of vulcanization were compounded with only the essential ingredients and heat-cured. The compounding formulas are shown in table 1. Because Vistanex is not a vulcanizable material, no compounding ingredients were added to it.

TABLE 1.—*Compounding formulas*

[Each column represents a separate compound]

Material	Parts by weight			
Smoked sheet rubber	100			
Perbunan		100		
Neoprene *G*			100	
Thiokol *Dx*				100
Sulfur	4	1		
Zinc oxide	5	5	5	10
Magnesium oxide			4	
Mercaptobenzothiazol (Captax)	1			
Benzothiazyl disulfide (Altax)		1		0.25
Diphenylguanidine				.1
Phenyl-β-naphthylamine (Neozone *D*)	1		2	

The method of determining permeability and the conditions of test were those which have been previously described.[1] It was assumed in all cases that the rate of permeation in mass per unit time is proportional to the partial pressure of the gas and inversely proportional to the thickness of film. Permeability is expressed herein as milliliters of hydrogen which penetrates a film 1 cm thick over an area of 1 cm^2 in 1 minute. It was assumed that only a negligible partial pressure of hydrogen exists on the low pressure side; then the permeability in volume of hydrogen (at the initial pressure) is independent of that pressure. The effect of temperature was found to be characteristic of each material and was included in the study.

III. EXPERIMENTAL RESULTS

In table 2 are shown the permeabilities obtained at 25° C, the temperature at which determinations on balloon fabrics are customarily made. Table 3 contains the rates of permeation at various temperatures, ranging generally from below 10° C to slightly above 40° C. The exponential character of the temperature-permeability relationship is shown by the curves in figure 1, in which the logarithm of the permeability is plotted with respect to the reciprocal of the absolute temperature.

TABLE 2.—*Permeabilities to hydrogen at 25° C*

Material	Permeability
	ml cm cm^{-2} min $^{-1}\times10^{8}$
Rubber	22.8
Perbunan	14.4
Neoprene *G*	5.4
Vistanex	2.6
Thiokol *Dx*	1.9
Pliofilm	0.4

[1] Theron P. Sager and Max Sucher, J. Research NBS **22**, 71 (1939) RP1166.

TABLE 3.—*Variation of permeability with temperature*

Temperature of test	Permeability to hydrogen at $t°$ C	Temperature of test	Permeability to hydrogen at $t°C$
RUBBER		VISTANEX	
°C	ml cm cm^{-2}min^{-1}×10^{+6}	°C	ml cm cm^{-2}min^{-1}×10^{+6}
6.0	9.8	1.0	0.73
10.0	11.8	4.4	.87
11.0	12.3	11.0	1.31
14.0	13.5	14.0	1.75
16.4	15.7	25.0	2.62
24.0	22.8	26.0	2.90
25.5	22.9	34.0	4.30
34.0	31.1	42.0	7.00
42.0	42.0		
PERBUNAN		THIOKOL *Dx*	
4.5	4.61	14.0	1.14
10.9	6.04	25.0	1.92
13.8	7.70	34.0	2.97
25.0	14.4	42.0	3.98
34.0	20.5		
42.0	29.0	PLIOFILM	
NEOPRENE *G*		3.8	0.13
		10.8	.21
9.0	2.27	14.4	.26
14.0	2.84	25.0	.44
25.0	5.40	34.0	.68
34.0	8.06	35.0	.79
42.0	11.6	42.0	1.26

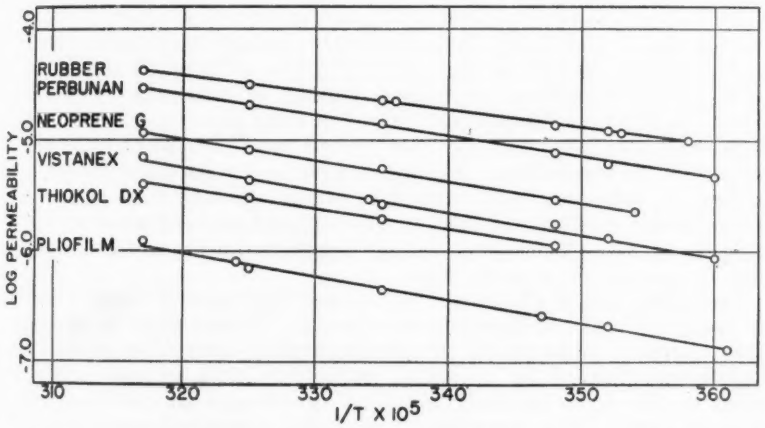

FIGURE 1.—*Relation between logarithm of permeability and reciprocal of absolute temperature.*

IV. DISCUSSION

The exponential increase in permeability with increasing temperature has been interpreted upon the basis of chemical kinetics. The straight lines obtained in figure 1 are evidence that the velocities of permeation are proportional to the quantity $e^{-E/RT}$, in which E is the activation energy of permeability. In table 4 are shown the values

for E which were computed from the slopes of the curves in figure 1. The values for rubber, chloroprene, and butadiene-acrylonitrile polymer have also been determined by Barrer,[2] with whose results these are in substantial agreement.

TABLE 4.—*Activation energies of permeability for hydrogen*

Material	Activation energy	Material	Activation energy
	cal/mole		*cal/mole*
Rubber	6,800	Vistanex	9,200
Perbunan	8,400	Thiokol *Dx*	8,400
Neoprene *G*	8,900	Pliofilm	9,500

The process of permeation involves the combined action of absorption of the gas by the solid and diffusion or movement of the gas from one point to another in the material. In order for a molecule of gas, located at any point in a solid, to undergo a change of environment, it is necessary that an amount of energy be furnished. Two possible circumstances may govern the consumption of this energy. Energy may be utilized in lessening the binding attraction of the solid for the gas or it may be employed in overcoming the repulsive force encountered as the gas molecule attempts to produce for itself a position or "hole" within the molecular network. In the case of these materials the likelihood of the latter as the predominant factor appears to be the greater. Hence it appears likely that differences in their permeabilities are largely determined by the structural characteristics on a molecular scale of the individual substances.

An indication of the effect of molecular structure upon the rate of permeation is shown by the comparative behavior of rubber and the hydrocarbons of balata and gutta-percha. The latter are identical with the hydrocarbon of natural rubber in chemical composition. They are however distinctly different in their physical characteristics. Rubber is amorphous in the unstretched condition whereas the other materials are crystalline. Balata and gutta-percha differ from rubber in density, softening point, and the viscosity of their solutions. They are regarded as stereoisomers of rubber, and in diagrammatic representations of the two forms, rubber is assigned a *cis* and gutta-percha and balata a *trans* arrangement.

The difference in the behavior toward hydrogen of these materials is shown by the following experiment. Balata and gutta-percha hydrocarbons, from which the accompanying nonrubber constituents had been removed by repeated extractions with acetone, were applied in the form of their solutions in toluene to two portions of balloon cloth. The amounts of material deposited upon the cloth upon evaporation of the solvent were of approximately the same weight per unit of area. A film of a "pure gum" rubber compound was similarly applied to a third portion of the same cloth. The permeabilities to hydrogen of the three fabrics were determined at 25° C. The values obtained and the weights of coatings are shown in table 5. Since the densities of these substances are not appreciably different, the permeabilities obtained on films of about the same weight per unit area are practically comparable.

[2] R. M. Barrer, Trans. Faraday Soc. 35, 637 (1939).

TABLE 5.—*Comparison of the permeabilities of fabrics coated with rubber, balata, and gutta-percha*

Material	Weight of coating	Permeability to hydrogen
	$g\ m^{-2}$	*Liter* m^{-2} $(24\ hr)^{-1}$
Rubber	123.0	13.4
Balata	125.4	1.7
Gutta-percha	98.3	2.2

Results which have been obtained from X-ray and electron diffraction studies of linear polymers [3] indicate that structural differences may exist between natural rubber and synthetic polymers which are similar to those which determine the distinctive characteristics of rubber and substances such as balata, and which may largely account for the differences in the permeability of these materials.

It is obvious that permeability alone does not wholly determine the relative utility of these materials for flexible gas-containing structures. Other factors which equally determine their usefulness are tensile strength, elongation, permanent deformation, resistance to natural aging, continued polymerization or depolymerization, and behavior at extremes of temperature. Most of the properties of the materials which have been considered here are known or are rapidly becoming so. They all possess certain characteristics which render them particularly useful in definite fields for which they were designed. In their present stage of development no one of them represents the ideal in every respect for the construction of gas containers. It has been observed, however, that changes in the physical characteristics of such materials, which are produced through changes in chemical composition, methods of preparation, or the nature and amounts of their compounding ingredients, are frequently not accompanied by any appreciable change in their behavior toward gases. The rate of permeation of uncured rubber, for example, differs but little from that of the fully vulcanized material, despite the extensive changes produced in other properties. The permeability of Neoprene *G* is but slightly higher than that of Neoprene *E*. (See footnote 1.) That of Thiokol *Dx* is of about the same order as that of other types of this material.[4] For this reason materials which are deficient only in certain physical characteristics may be capable of being improved in this respect without serious impairment of their low rates of permeation.

Since it is becoming increasingly evident that neither the property of elastic extensibility nor impedance to the passage of gases is restricted to any sharply defined group of substances, there is the further possibility that some new type of polymer may yield an even more desirable material.

WASHINGTON, June 17, 1940.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1328

Part of Journal of Research of the National Bureau of Standards, Volume 25, September 1940

ELECTRODE POTENTIAL MEASUREMENTS AS A MEANS OF STUDYING THE CORROSION CHARACTERISTICS OF WROUGHT ALUMINUM ALLOYS OF THE DURALUMIN TYPE

By Hugh L. Logan

ABSTRACT

A study was made of the reliability of basing predictions of the susceptibility of the duralumin-type alloys to intercrystalline corrosion on electrode-potential measurements. These measurements were made in a potassium chloride solution against a saturated calomel electrode.

A condenser, charged by this galvanic cell, was discharged through a calibrated ballistic galvanometer. A comparison of the measured potentials with the result of corrosion tests on the same specimens showed that materials with electrode potentials more negative than −0.657 volt at 25° C were in general susceptible to intercrystalline corrosion, and those with less negative potentials were immune to this type of corrosion. Measurements with a potentiometer are less reliable, but may be used to determine whether the potential is above or below −0.657 volt.

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I. INTRODUCTION

The aluminum alloys of the duralumin type attain their high strength and other desirable physical properties by heat-treatment, usually performed in three stages: (a) The alloy is heated at approximately 500° C for a sufficiently long period to bring most of the alloying constituents into a stage of homogeneous solid solution; (b) the material is cooled rapidly to room temperature; and (c) it is aged for several days.

The distinguishing feature of the duralumin alloys is the improvement in the properties of the quenched alloy on aging at room temperature. In some aluminum alloys, "accelerated aging" is necessary, that is, the quenched alloy must be reheated, above room temperature. The designation "duralumin type" is restricted in this report to those heat-treatable aluminum alloys that do not require accelerated aging.

None of the aluminum alloys are entirely immune to corrosion, although this may be negligible under many conditions of service. The rate of corrosion varies according to the environment, the composition of the alloy, and especially the heat-treatment. The rate at which the material is cooled from the solution-treatment temperature (step b above) is very important in determining the character of any corrosion that may occur. Corrosion of material that has been cooled slowly by quenching in hot water is mostly confined to the grain boundaries and may penetrate rather deeply without leaving any marked evidence of corrosion on the surface. Corrosion of this type may be very damaging to the ductility and strength of the material, especially of sheets.

The same alloy, however, if cooled more rapidly, by quenching in cold water, is practically immune to the intercrystalline type of corrosion, although its initial tensile strength and other properties do not differ essentially from those produced by quenching in hot water. Any corrosion that occurs is generally of the pitting type, which has a much less damaging effect on the tensile strength, ductility, and other physical properties. The damage to the physical properties of duralumin by corrosion varies with the intensity of the intercrystalline attack. Material with only traces of intercrystalline attack may be damaged no more severely than that corroded by pitting.

To illustrate these two types of corrosion, identical specimens from a single sheet were cooled from the solution-heat-treatment temperature by quenching in water at 94° C and 26° C, respectively, and were examined after immersion for equal periods in a corroding solution. The slowly cooled material showed severe attack along the grain boundaries. Its ductility, as measured by the elongation (2-in. gage length) of the specimen broken in tension, was reduced from 21 percent, which was characteristic of the uncorroded condition, to 4.5 percent. Similarly, the ultimate tensile strength was reduced from 66,000 lb/in.^{2} (in the uncorroded condition) to 40,000 lb/in.^{2} The companion specimen that was cooled rapidly, by quenching in water at room temperature, exhibited only the pitting type of corrosion. The elongation of this specimen after corrosion was 9.4 percent and the ultimate tensile strength was 57,500 lb/in.^{2}

It is evident that a method of testing to indicate the type of corrosive attack that might be expected for any specific lot of a heat-treated aluminum alloy would serve a very useful purpose. The method usually employed involves immersion in a sodium chloride solution containing hydrogen peroxide, and examining the microstructure of the corroded material to determine the character of the attack. This method is time-consuming and necessitates the cutting of specimens from the article. A more rapid and nondestructive test has long been sought.

The electrode potential of an alloy of the duralumin type varies with the heat-treatment and particularly with the rate at which the alloy has been cooled after the solution-heat treatment. Attempts [1] [2] have been made to use this potential to predict the type of corrosion to which the material may be susceptible. This study was conducted to determine the reliability of such predictions.

[1] Private Communication from F. P. Somers, Naval Aircraft Factory, Philadelphia, Pa.
[2] Private communication from E. H. Dix, Jr., Aluminum Company of America, New Kensington, Pa.

II. MATERIALS

Alloys of the duralumin type contain as essential alloying constituents, copper, magnesium, manganese, and silicon. Two commercial aluminum alloys, 17S and 24S, with type compositions given in table 1, were used in this study.

TABLE 1.—*Type compositions of commercial alloys of the duralumin type*

	17S	24S
	Percent	*Percent*
Copper	4.0	4.4
Magnesium	0.5	1.5
Manganese	0.5	0.5
Iron	[a] 1.0	[b] 0.5
Silicon	[a] 0.8	[b] 0.5
Other elements, total	[a] 0.38	[b] 0.38
Aluminum	Remainder	Remainder

[a] Maximum permitted in Federal Specification QQ-A-353a.
[b] Maximum permitted in Federal Specification QQ-A-355.

The material was in sheet form, 0.020 to 0.064 in. thick. Most of the 24S alloy was from 18 lots of commercially heat-treated aluminum-alloy sheet. The remainder was commercial sheet heat-treated at the National Bureau of Standards. The 17S alloy included commercial sheets heat-treated at the National Bureau of Standards and commercially heat-treated sheet from two sources. Some heat-treated duralumin of German origin was used for comparison with the 17S material.

III. DETERMINATION OF ELECTRODE POTENTIALS

The electrode potential of each metal in a saturated solution of potassium chloride was measured against a saturated calomel electrode. Each reported potential is the emf of a cell in which a small area (0.8 to 1 cm^2) of the metal surface was in contact with the potassium chloride solution that in turn was connected to the calomel electrode. As in all cases the aluminum was negative with respect to the mercury of the half cell, the "electrode potential" of the aluminum is reported as "negative." An increase in the numerical value of this potential represents a more negative potential and vice versa.

1. PREPARATION OF SURFACE OF SPECIMEN

The surface condition of the metal after the heat-treatment varied considerably among specimens from the same lot. In some cases the electrode potential of a specimen was made less negative by the removal of the surface film produced during the heat-treatment. In order to make the potential measurements on all specimens under similar conditions, the surface films were removed with fine emery paper. With careful surface preparation, reproducible results could be obtained for repeated determinations on the same specimen. Vigorous or long-continued abrasion of the surface made the solution potential less negative. Failure to remove all the initial surface film caused a trend in the opposite direction, that is, the measurements were more electronegative than if the surface had been properly prepared.

In order to obtain reproducible results, no electrode potentials were determined until at least 6 minutes after the surface preparation had been completed. The potentials immediately determined ranged from −0.90 to −1.00 volt. The potential decreased in magnitude with time and approached a constant value in the range −0.628 to −0.755 volt in from 4 to 6 minutes after the surface preparation had been completed.

Although the tensile strength and hardness of these alloys is increased by aging after the heat treatment, the solution potential remained constant.

2. THE CALOMEL ELECTRODE [3]

In order that the test could be applied directly to metal in a finished structure, the calomel electrode of the saturated potassium chloride type shown in figure 1 was constructed. Fresh solution was supplied from the reservoir for each reading. The vent was used to remove air bubbles from the bridge. The contact tip could be used in any position. The rubber gasket served to retain the solution in position, to make the area under test approximately constant, and to prevent scratching the surface film of the alloy while under test. If this surface was scratched, a very high electronegative potential was obtained.

The apparatus and method of making contact through the liquid bridge are shown in figure 2. The electrode was kept at 25° ±0.1° C in a Dewar flask.

The emf of the cell, calomel electrode–aluminum alloy, increased with temperature. For heat-treated 17S and 24S alloys, the average value of this change from 16° to 36° C, with the electrode at 25° C, was 1.45 millivolts (or for practical purposes, 1.5 millivolts) per degree C.

3. BALLISTIC-GALVANOMETER METHOD

The reaction between the potassium chloride solution and the alloy resulted in rapid and unpredictable variations of the potential as measured directly by a potentiometer. This difficulty was overcome by using a condenser and ballistic galvanometer. The galvanic cell containing the aluminum alloy was used to charge a 4-microfarad condenser, and the emf of the cell was then determined by discharging the condenser through a calibrated ballistic galvanometer. This calibration was made by discharging the condenser, after it had been charged to various known potentials, through the galvanometer. Measurements were made with a precision of 1 millivolt. The usual variation of three to five separate potential determinations made on a properly heat-treated specimen of the 24S alloy was 5 millivolts, and the averages of successive sets of readings on the same specimen checked to about 3 millivolts. The circuit used for the potential measurements and also the auxiliary circuit for calibrating the galvanometer are shown in figure 3.

[3] The use of the calomel electrode to predict susceptibility of duralumin to intercrystalline corrosion was called to the author's attention by F. P. Somers of the Naval Aircraft Factory, Philadelphia, Pa. The electrode and the ballistic galvanometer method described in this paper were used to overcome certain difficulties experienced in using the Somers method and electrode.

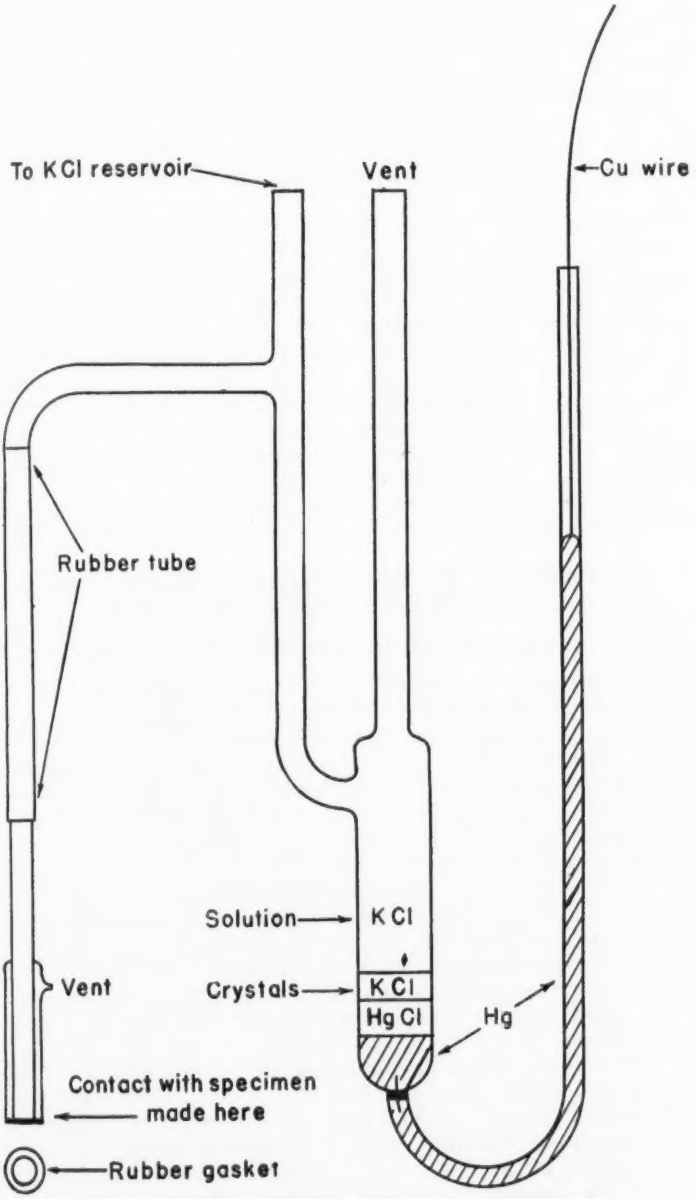

FIGURE 1.—*Schematic diagram of calomel electrode.*

4. POTENTIOMETER METHOD

Galvanometers of the sensitivity required for measurement of the solution potentials by the ballistic-galvanometer method are not rugged enough to be readily portable. Hence, ballistic-galvanometer measurements can be made only under conditions permitting a solid and semipermanent mounting for the galvanometer. It is desirable in some instances to make potential measurements on metal in a structure under conditions that would not permit the use of a ballistic galvanometer. Under such conditions the potentiometer method is useful.

Although it was not possible to determine accurately the emf of the galvanic cell by means of a potentiometer, useful indications were obtained by the following procedure. A "critical" potential was selected from a comparison of the potential determined with the ballistic galvanometer with the results of accelerated-corrosion tests on the same material. It was then possible to determine from the direction of the galvanometer deflection of the potentiometer whether the potential of a particular specimen was above or below the "critical" potential to which the potentiometer was adjusted. The results most consistent with those of the accelerated-corrosion tests were obtained by recording the galvanometer deflection after a relatively steady state had developed, which was usually in from 10 to 20 seconds after connection was made between the specimen and the calomel electrode.

IV. COMPARISON OF ELECTRODE POTENTIALS WITH RESULTS OF CORROSION TESTS

1. SUSCEPTIBILITY TO INTERCRYSTALLINE CORROSION

The susceptibility to intercrystalline corrosion of the heat-treated alloys was determined by metallographic examination of two or more coupons from each specimen that had been subjected to an accelerated-corrosion test. This was done by immersing the coupons at an angle of approximately 20° to the horizontal for 48 or 72 hours in a solution containing 57 g of NaCl and 100 ml of 3-percent H_2O_2 per liter. Equally satisfactory results were obtained whether the specimens, cut from clean material, were or were not first degreased in a benzol-acetone mixture. The corroding solution was renewed each 24 hours. The immersion period depended upon the thickness of the specimens. Those 0.050 in. or less in thickness were immersed for 48 hours and those 0.064 in. thick for 72 hours. During the corrosion test no attempt was made to maintain a constant temperature. The test was conducted at room temperature, which varied somewhat throughout each day.

For the metallographic examination, packs of 12 to 20 of the corroded coupons were bolted together, with a sheet of uncorroded metal at each end of the pack. The pack of specimens was then polished for metallographic examination of transverse sections.

All the alloys of the duralumin type were attacked in some manner by the sodium chloride–hydrogen peroxide solution. Specimens that had been cooled rapidly from the solution-heat-treatment temperature were subject only to pitting, but those that had been cooled slowly were susceptible to intercrystalline attack.

Specimens found to contain even limited areas of intercrystalline attack of the extent and severity shown in *C* and *D*, figure 4, and also

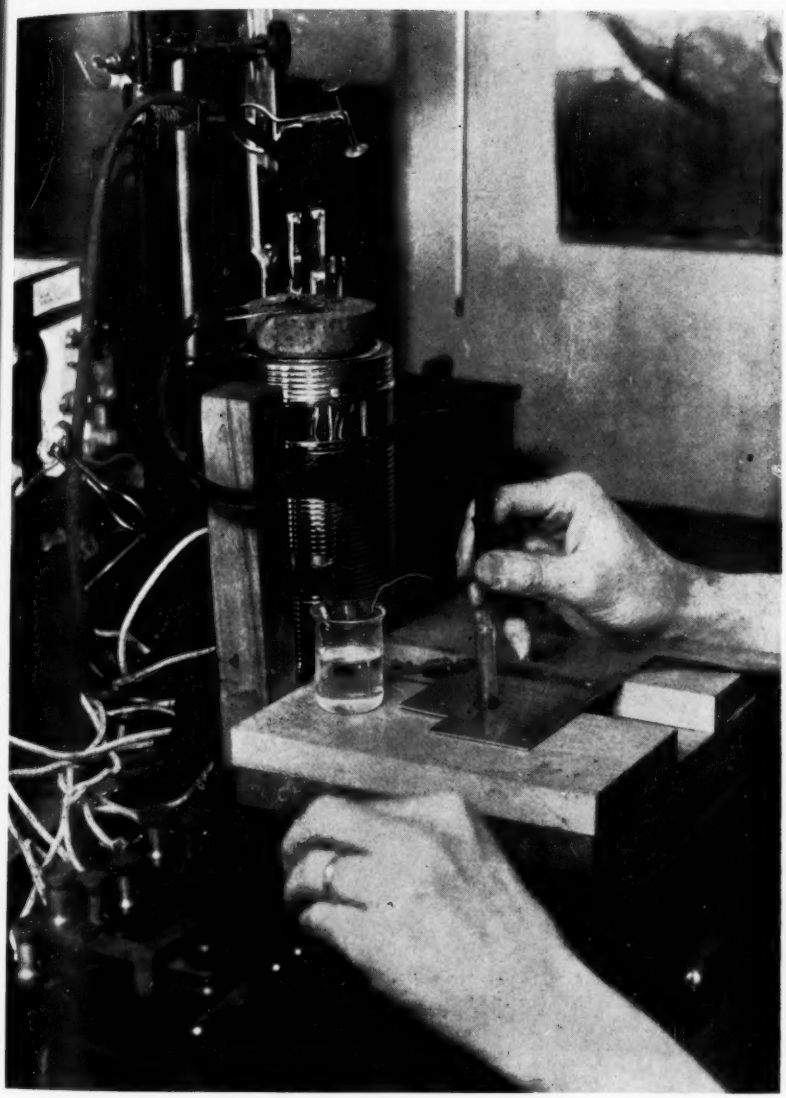

FIGURE 2.—*Calomel electrode in use.*

The electrode is contained in the Dewar flask.

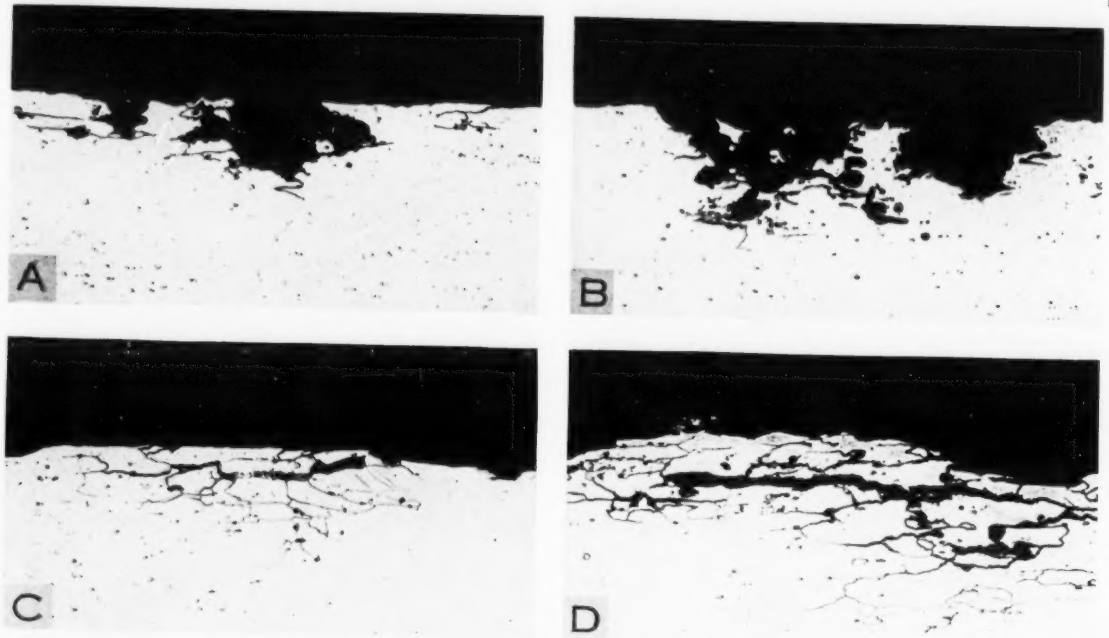

FIGURE 4.—*Typical examples of intercrystalline corrosion in 24S alloy.*

Photomicrographs show portions of cross-sections of corroded sheet; unetched. ×100.

A and *B*, "traces" of intercrystalline corrosion at bottoms of pits. *C* and *D*, "severe" intercrystalline corrosion.

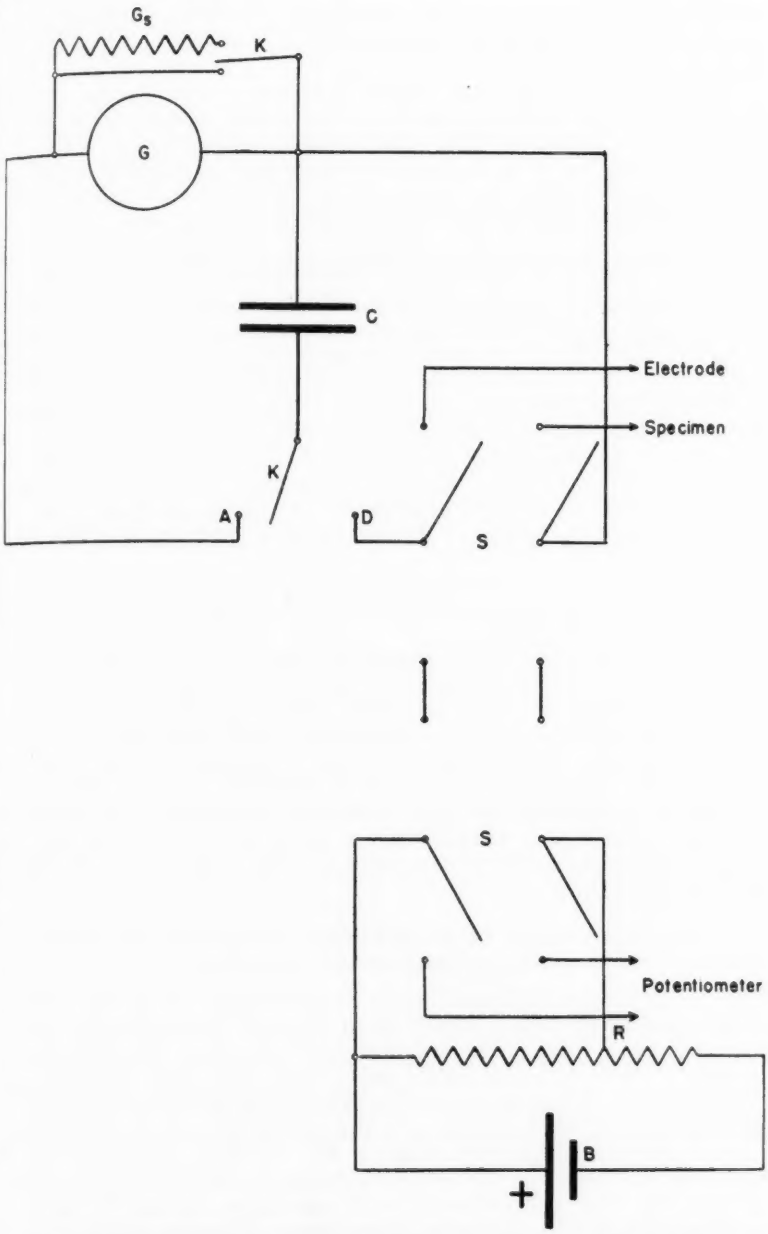

FIGURE 3.—*Wiring diagram for potential measurements with ballistic galvanometer.*

B, 1.5-volt battery; *C*, 4-microfarad condenser; *G*, ballistic galvanometer; G_s, shunt; *K*, keys; *R*, 1500-ohm radio potentiometer; *S*, switches.

those showing less severe but generally distributed intercrystalline attack were classified as susceptible to "severe" intercrystalline corrosion.

Corrosive attack that was primarily of the pitting type but included areas of intercrystalline attack of the degree shown in *A* and *B*, figure 4, was classed as "traces" of intercrystalline attack. The same term was applied to specimens that showed a single isolated area of severe intercrystalline corrosion on one of several specimens from a given group with the remainder containing only pitting.

2. DETERMINATION OF CRITICAL-SOLUTION POTENTIAL

The potentials of 404 specimens of heat-treated 24S alloy, determined with the ballistic galvanometer, ranged from −0.628 to −0.755 volt. The "critical" potential within this range would be that value that was more electronegative than the potentials of all specimens immune to intercrystalline corrosion and less negative than the potentials of all specimens susceptible to intercrystalline corrosion. In attempting to correlate the potential values and the results of the corrosion tests, the maximum rather than the average potential obtained on each specimen gave the most satisfactory correlation. On this basis the specimens were tentatively divided into three groups:

1. The maximum potentials were more electronegative than −0.672 volt. All these specimens were susceptible to intercrystalline corrosion, usually severe.
2. The maximum potentials were less than −0.648 volt. All these specimens were immune to intercrystalline corrosion.
3. The maximum potentials were between −0.672 and −0.648 volt. The behavior of these specimens, with respect to intercrystalline corrosion, differed, as some were immune to intercrystalline attack, and others were susceptible to "traces" or severe attack.

Further analysis of the data indicated that of the possible values between −0.648 and −0.672 volt, a value of −0.657 volt, which is slightly below the mean, best satisfies the above criteria for the critical solution potential.

3. COMPARISON OF ELECTRODE PREDICTIONS WITH METALLOGRAPHIC FINDINGS

In order to check the reliability of predictions based on a critical value of −0.657 volt (derived from ballistic measurements on 404 samples of 24S alloy), the potentials and corrosion behavior of other specimens were studied. Potentials were measured with the galvanometer on 21 specimens of the 17S alloy and 25 specimens of the German duralumin, in addition to the 404 specimens of the 24S alloy.

Using the potentiometer method, the relative magnitudes of the measured potential and the critical solution potential, −0.657−0.0015 (T–25) volt, were determined for 200 specimens of the 24S alloy, 42 specimens of the 17S alloy, and 25 specimens of the German duralumin.

Measurements of the potential of each specimen were made at three to five locations on surfaces prepared as described in section III. If any potential measurement was more negative than −0.657 volt (when corrected to 25° C), the surface preparation was repeated and an additional set of readings was made. If, in the second set of readings, any value was greater than −0.657 volt, the specimen was

classified as susceptible to intercrystalline corrosion in some degree. Some materials that were susceptible only to traces of intercrystalline corrosion had potentials as negative as −0.690 volt, which shows that it is not possible to predict the degree of intercrystalline corrosion from potential measurements.

A comparison of the predictions of susceptibility to intercrystalline corrosion with the microscopic examinations of corroded coupons of the same specimen is given in table 2:

TABLE 2.—*Comparison of the predictions of susceptibility to intercrystalline corrosion from potential measurements and the results of the accelerated corrosion tests*

Material	Method of determining potential	Number of specimens examined	Predictions based on potential measurement		Predictions confirmed by microscopic examination of corroded specimens		Percentage of correct predictions
			Specimens susceptible to intercrystalline corrosion	Specimens immune to intercrystalline corrosion	Specimens susceptible to intercrystalline corrosion	Specimens immune to intercrystalline corrosion	
24S	Ballistic galvanometer	404	154	250	126	227	87
Do	Potentiometer	200	46	154	39	132	85
17S	Ballistic galvanometer	21	13	8	12	7	90
Do	Potentiometer	42	17	25	12	23	86
German duralumin	Ballistic galvanometer	25	23	2	21	1	88
Do	Potentiometer	25	19	6	19	3	88

The percentages of correct predictions in table 2 refer to all degrees of intercrystalline corrosion. As stated, it is not generally possible to predict the degree of intercrystalline attack from potential measurements. The data in table 3 show that potential measurements with the ballistic method yielded correct predictions for nearly all the specimens that showed severe intercrystalline corrosion and for a large proportion of those that showed traces of corrosion. For the latter class, the potentiometer measurements are less reliable.

TABLE 3.—*Proportion of specimens found to be susceptible to severe or traces of intercrystalline attack in the corrosion test that was predicted from potential measurements to be susceptible to intercrystalline attack*

Material	Method of determining solution potential	Number of specimens examined	Rating of material on basis of results of corrosion tests. Number of specimens susceptible to intercrystalline corrosion		Specimens predicted to be susceptible to intercrystalline corrosion in some degree that were subject to			
					Severe attack		Traces of attack	
			Severe attack	Traces of attack	Number of specimens	Percent	Number of specimens	Percent
24S	Ballistic galvanometer	404	74	76	73	98.6	53	69.7
Do	Potentiometer	200	33	28	30	90.9	9	32.1
17S	Ballistic galvanometer	21	9	4	9	100	3	75
Do	Potentiometer	42	11	3	11	100	1	33.3
German duralumin	Ballistic galvanometer	25	10	12	9	90	12	100
Do	Potentiometer	25	10	12	8	80	11	91.7

Although it may be desirable that any method of separating specimens of aluminum alloys, on the basis of resistance to corrosive attack, should correctly indicate all materials that are at all susceptible to intercrystalline attack, it is more important that the predictions be correct for those samples that are susceptible to severe intercrystalline attack.

Where a readily portable instrument is required, valuable indications of the susceptibility of material to intercrystalline corrosion can be obtained by means of the potentiometer, but the ballistic-galvanometer method should be used if feasible.

The lack of complete agreement between the predictions and the results of the corrosion tests can be attributed in part to:

Nonuniform heat-treatment of specimens.—On certain specimens, some areas were susceptible to intercrystalline attack while others were not. Complete agreement between the potential measurements and the results of the corrosion test can be expected only if potential measurements were made upon the areas chosen for microscopic examination after immersion in the corroding solution. Usually, the potential measurements and corrosion tests were made upon different parts of the specimen.

Some specimens heat-treated at temperatures below the recommended range, or heat-treated for a very short time in the recommended range, had more negative potentials than −0.657 volt, although the specimens were immune to intercrystalline attack.

Improper surface preparation.—In some cases, failure to remove all the surface films that had been produced during heat-treatment resulted in potentials more negative than the critical potential, although the material when corroded showed only pitting. Conversely, too vigorous abrasion of the surface to remove the film lowered the potentials of certain specimens, known to be susceptible to intercrystalline corrosion, to a value below the critical potential.

Experiments on materials of known composition indicated that differences in copper content are not an appreciable source of error in this work.

Potential measurements as a means of predicting susceptibility of aluminum alloys to intercrystalline corrosion, made by persons with training and experience in physical chemistry, furnish a rapid, reliable method of checking heat-treatment. It is possible by this method, without destroying the structure, to predict with a high degree of certainty whether material in a structure such as an airplane wing is susceptible to intercrystalline corrosion. On the other hand, predictions based on potential measurements do not, in general, indicate the degree of susceptibility to intercrystalline attack. In its present state of development, this method is not one to be entrusted to inspectors who lack broad training in science. It is therefore recommended that this method be used to supplement rather than to replace the present accelerated-corrosion tests.

V. SUMMARY

1. The reliability of predictions of susceptibility of duralumin-type alloys to intercrystalline corrosion from measurements of electrochemical potentials was investigated.

2. The potential determinations are most accurately made by charging a condenser, by means of a galvanic cell consisting of a calomel electrode and the alloy, and discharging the condenser through a calibrated ballistic galvanometer.

3. The relative potential of a material can be determined by setting a potentiometer to a predetermined potential and determining from the galvanometer deflection whether the potential is greater or less than the chosen value.

4. The predicted susceptibilities to intercrystalline corrosion were compared with the results of accelerated-corrosion tests, carried out by immersing specimens for 48 to 72 hours in a solution of sodium chloride and hydrogen peroxide.

5. A potential of $-0.657-0.0015(T-25°$ C) volt was selected as the critical solution potential. Intercrystalline corrosion in some degree was correctly predicted from ballistic galvanometer measurements in 98.6 percent of the 24ST specimens that were rated by corrosion tests as subject to severe intercrystalline corrosion. Susceptibility or immunity to intercrystalline attack was correctly predicted in 87 percent of all specimens.

6. Intercrystalline corrosion in some degree was correctly predicted from potential measurements with the potentiometer method on 91 percent of 24ST specimens that were susceptible to severe intercrystalline corrosion. Correct predictions of susceptibility or immunity of material to intercrystalline corrosion were made on 85.5 percent of all the specimens.

7. There was insufficient material available to determine whether 0.657 volt is a satisfactory critical potential for 17S and German duralumin.

8. It is recommended that the potential method of predicting susceptibility to intercrystalline corrosion be used by scientifically trained personnel to supplement rather than to replace the present accelerated corrosion test.

WASHINGTON, June 1, 1940.

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

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AN IMPROVED RADIO SONDE AND ITS PERFORMANCE

By Harry Diamond, Wilbur S. Hinman, Jr., Francis W. Dunmore, and Evan G. Lapham

ABSTRACT

The radio sonde (radiometeorograph) described in Research Paper RP1082 [1] has emerged from the laboratory and been put into daily service in a widespread network of stations by the Government aerological services. The present paper describes improvements in component elements of the radio-sonde system and discusses performance. Actual performance in service is stressed. The major improvement introduced is in the element for measuring relative humidity. Laboratory and flight data on the accuracy of measurement with this element at temperatures down to −60° C are presented. The improved radio sonde is shown to be capable of measuring barometric pressure to an accuracy of 5 millibars, temperature to an accuracy of 0.75 degree centigrade, and relative humidity to an accuracy of 5 percent.

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[1] H. Diamond, W. S. Hinman, Jr., and F. W. Dunmore, J. Research NBS **20**, 369 (1938) RP1082.

I. INTRODUCTION

An earlier paper [1] [2] described a method of upper-air radio soundings for sending down from small unmanned balloons information on the barometric pressures, air temperatures, and relative humidities encountered. This method has been the subject of continued experimental work since the preparation of the earlier paper and has been adopted for routine use in an extensive network of weather-reporting stations. The present paper describes the more recent improvements in the system and gives an analysis of performance. Details of improvements and performance treated in other publications [2] are not covered except as found necessary to present a complete description.

As in the original development, the work on improvement of the system was carried on under the sponsorship of the Bureau of Aeronautics, United States Navy Department. Close cooperation was had in the work with Julien P. Friez & Sons, engineers of that company contributing many practical features to the commercial design of the radio sonde and ground-station equipment. The recorder shown in figure 7 is a development of the Friez company.

II. SERVICE REQUIREMENTS AND PERFORMANCE

Service use of the radio sonde began at the Naval Air Station, Anacostia, D. C., on June 1, 1938, and was extended to 12 Weather Bureau, Navy Department, and Coast Guard stations during the fiscal year 1939. The regularity and reliability of the results obtained warranted considerable expansion of the system, so that some 45 stations are in present operation, representing an annual use of 15,000 instruments. Figure 1 shows the network of stations in use. About two-thirds of these stations are operated by the Weather Bureau and the remainder by other agencies, such as the Navy Department, Coast Guard, Army, etc.; some of the stations shown operate seasonally. Because of the use of small unmanned balloons, soundings may be made from shipboard stations or from small islands where it would be impractical to use airplanes for carrying up recording instruments (the practice prior to the advent of the radio sonde). Thus, regular soundings have been made from Coast Guard cutters in the Newfoundland ice fields and in the South Atlantic as a service for the transatlantic air route.

1. REGULARITY OF OPERATION AND HEIGHTS OF SOUNDINGS

Maximum operating efficiency of the network of stations shown in figure 1 imposes the following three requirements: (1) The soundings must be made on a regular, uninterrupted schedule. (2) They must attain heights well into the stratosphere, of the order of at least 10 to 15 kilometers, since air mass movements occur up to these heights. (3) The data must be available for dispatching to central offices in time for the morning forecast, that is before 7 a. m. EST. The improvement in regularity of operation and in the maximum heights of the soundings, afforded by the radio sonde over the airplane method, is indicated in table 1.

The data tabulated compare the results obtained with the radio sonde for August to October, 1938, inclusive (a few months after

[1] Figures in brackets indicate the literature references at the end of this paper.

radio-sonde operation was inaugurated), and with the airplane method for the same months of the previous year. The two stations chosen, Oakland, Calif., and Sault Ste. Marie, Mich., represent locations where flying conditions are notably different, particularly during the late fall and winter months. The effect of adverse weather conditions upon the number of useful soundings with the airplane method is

FIGURE 1.—*Network of aerological stations at which radio soundings are made.*

evident from the fourth column of the table. Because of adverse weather, airplane soundings at Sault Ste. Marie during the late fall and winter had limited utility despite the importance of information from this station during the formation of cold waves. There is no marked equivalent effect in the case of the radio sonde; soundings with this method are possible in practically all types of weather except during very strong winds and conditions conducive to ice formation on the balloon.

TABLE 1.—*Comparison of regularity and maximum heights of soundings with airplane and radio sondes*

Month	Method of sounding	Number of soundings made	Number of soundings providing data in time for the morning forecast	Average of maximum heights attained, kilometers
OAKLAND, CALIF.				
Aug. 1937	Airplane	29	29	5.2
Aug. 1938	Radio sonde	30	30	14.3
Sept. 1937	Airplane	30	30	5.1
Sept. 1938	Radio sonde	30	30	18.9
Oct. 1937	Airplane	30	25	5.2
Oct. 1938	Radio sonde	30	30	15.8
SAULT STE. MARIE, MICH.				
Aug. 1937	Airplane	31	20	5.3
Aug. 1938	Radio sonde	30	30	12.6
Sept. 1937	Airplane	30	19	5.0
Sept. 1938	Radio sonde	29	29	16.0
Oct. 1937	Airplane	29	13	4.8
Oct. 1938	Radio sonde	31	31	17.8

Further information on the heights attained with the radio-sonde method is given in figure 2, which summarizes data [3] for 5,222 soundings. Approximately 70 percent of the soundings reached 15 kilometers. Analysis of the data (not given here) shows a marked seasonal variation of the maximum heights attained, greater heights being reached during August and September, when winds prevailing over the country have relatively low velocities, and lower heights being attained during January, February, and March, when prevailing wind velocities are relatively high. Thus, some 70 percent of the soundings reached 17 kilometers during August and September, whereas only 25 percent of them reached this altitude during January, February, and March. This would appear to indicate that the maximum heights attained have been primarily dependent on the distance range of radio reception, the stronger winds serving to carry the balloons farther away from the receiving station, often up to 200 kilometers at the ceiling height of the balloon. Commonly accepted limitations, such as type of balloon, weight of the instrument, etc., are evidently only of secondary importance. Hence, a practical expedient for increasing the height of soundings would be to increase the rate of ascent of the balloon from 175 meters per minute (as hitherto used) to about 300 meters per minute. Besides limiting wind drift, this would provide the additional advantage of decreasing the time taken for securing the required data.

An important limitation to the rate of balloon ascent practicable is the speed of response of the measuring elements in the radio sonde. All of the elements in the improved radio sonde permit using the higher rate of ascent specified. The important improvement in this respect lies in the electric hygrometer [3] for measuring relative humidity. Instruments using this device are employed at about one-fourth of the stations shown in figure 1 and are soon expected to replace the older type instruments, using hair hygrometers, at all the stations.

[3] Taken from Monthly Weather Review.

2. INSTRUMENT REQUIREMENTS

The instrument requirements for the radio-sonde system are rather severe. Measurements of pressure, temperature, and humidity are desired to heights up to 25 kilometers. In such excursions, the range of pressures encountered may be from 1,050 millibars at the surface to 25 millibars at the top, the range of temperatures from $+40°$ to $-90°$ C, and the range of humidities from 0- to 100-percent relative humidity. The present required accuracies of measurement are ± 5 millibars throughout the range of pressures, ± 0.75 degree

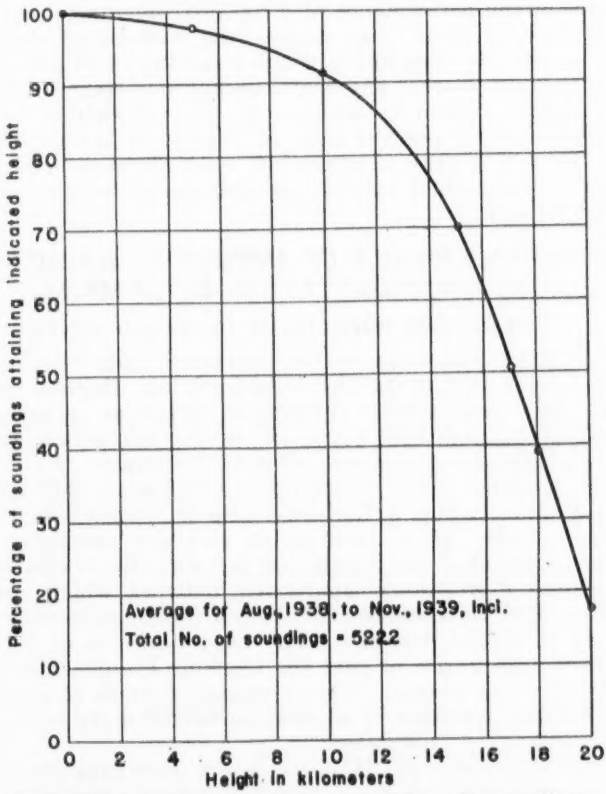

FIGURE 2.—*Analysis of heights attained by radio soundings.*

centigrade at temperatures above $-50°$ C and ± 5-percent relative humidity at temperatures above about $-20°$ C.

The very nature of the service imposes special practical requirements. Considerations of economy dictate that the cost of a radio sounding should not exceed the amount hitherto expended for an airplane sounding ($25 to $35). The weight of the instrument should be kept sufficiently low (of the order of 1 kilogram) to allow its being carried aloft by a balloon of reasonable size, 5 to 6 feet surface inflation diameter. Rugged construction is essential so that the instrument may be shipped by ordinary transportation methods from the factory to the far-flung stations of the network (see fig. 1), and stored at these stations until used, without upsetting the original calibrations. Ease

of handling by field personnel and minimum time for making the sounding and for evaluating the observations are additional conditions.

It will be evident from the foregoing considerations that the practicability of a radio-sonde design depends not only on its accuracy of measurement but also upon the ruggedness of the component elements and upon the possibilities of their manufacture by mass-production methods. The instrument to be described is fully capable of meeting all the requirements specified. The accuracies of the pressure and temperature observations in the field have been determined to be within the required tolerances, as will be shown later in the paper. An analysis of the performance of 5,200 instruments (using the hair-type hygrometer) shows that, despite the widespread dispersion of the stations and the customary rough handling in shipment, only 4 percent of the units were in any degree damaged in transit. Of a batch of 500 soundings, taken at random, 95 percent yielded satisfactory records, while only 5 percent were sufficiently defective to be called failures. During a year of operation, only about 1 percent of the soundings was cancelled because of instrument failures or adverse weather conditions.

III. GENERAL DETAILS OF IMPROVED RADIO-SONDE AND GROUND-STATION EQUIPMENT

1. OPERATING PRINCIPLES OF RADIO SONDE

The operating principles of the improved radio sonde may be understood by reference to the electric-circuit diagram shown in figure 3. The radio-sonde transmitter employs a conventional receiving-type vacuum tube (type 19) having two sets of triode elements in a single glass envelope. One of the triodes, C, is connected in a carrier oscillator circuit, operating at a frequency of 65 megacycles per second and feeding a half-wave dipole transmitting antenna. The second triode, M, is used in an auxiliary oscillatory circuit, oscillating at about 1 megacycle per second; this oscillator has in its grid circuit a resistance-capacitance network which operates to interrupt or block the oscillator at a rate inversely proportional to the time constant of the network. The capacitance is of fixed value, but the resistance varies so that the blocking frequency ranges from 10 to 200 cycles per second. This frequency is made to modulate the carrier oscillator, resulting in an emitted carrier wave having a variable audio-frequency modulation.

The temperature element [4] consists of a glass capillary tube filled with an electrolyte which has a high temperature coefficient of electrical resistance. Each element of the electric hygrometer [3] constitutes an electrical resistance formed by the leakage path across a thin film containing a hygroscopic salt between the two wires of a bifilar winding. It will be seen that the temperature tube and the electric hygrometer constitute electrical resistors which vary respectively in accordance with the temperature and relative humidity of the air to which they are exposed. Hence, when one or the other is connected in the grid circuit of the modulating oscillator to form the variable portion of the resistance in the resistance-capacitance network, the modulation frequency on the emitted carrier wave will be a measure of the temperature or humidity, respectively.

The pressure-switching unit performs two functions; one as a measuring instrument of barometric pressure in the specified range;

FIGURE 3.—*Electric-circuit arrangement of radio sonde.*

M = Modulating oscillator.
C = Carrier oscillator.
R_1 = 1,000 ohms.
R_2 = 40,000 ohms.
R_3 = 25,000 ohms.
R_4 = 1,000 ohms.
R_5 = 5,000 ohms.
R_6 = 1 megohm.

C_1 = 0.00025 microfarad.
C_2 = 0.07 microfarad.
C_3 = 0.05 microfarad.
C_4 = 0.00025 microfarad.
C_5 = 0.01 microfarad.
C_6 = 0.0001 microfarad.
C_7 = 0.00025 microfarad.

the other as a switch which connects into the resistance-capacitance circuit of the modulating oscillator, the temperature and humidity resistors and two fixed values of resistance known as the low and high reference resistors. The pressure arm carries a tapered contactor which bears against the polished face of a switching element at a position controlled by the ambient pressure. As the balloon rises into lower levels of pressure, the diaphragm expands laterally, thereby sweeping the contactor over the face of the switching element and making the desired connections.

The switching element consists of 80 metallic strips separated by insulating strips. The conducting strips are arranged in groups of four adjacent intermediate contacts, the adjacent groups being separated by wider index contacts. The intermediate conducting strips are all connected together and to the field coil of a miniature relay which is energized upon completion of a low-voltage circuit by contact of the pressure-arm contactor with any of the intermediate conducting strips. The grounded armature of the relay normally rests against its back contact, to which is connected one side of the temperature resistor. When the coil of the relay is energized, its armature bears against a front contact to which is connected one side of the humidity resistor.

By reference to figure 3, it will be evident that the relay operates to connect into the resistance-capacitance network of the modulating oscillator (in series with R_2 and R_1) either the resistance thermometer or the resistance hygrometer, depending upon whether the pressure-arm contactor bears against an insulating strip or an intermediate conducting strip of the switching element. The intermediate conducting strips are more conveniently referred to as humidity contacts, since the time constant of the resistance-capacitance network and, hence the modulating frequency of the radio-sonde transmitter, is controlled by the resistance hygrometer when the pressure-arm contactor bears against any one of these contacts.

The index conducting strips of the switching element are arranged in two groups; the members of one group are connected electrically to the junction of resistors R_2 and R_1, and the members of the second group to the junction of R_1 with the two measuring elements. Contacts of the first group, comprising contacts numbers 15, 30, 45, 60, and 75, are termed the high reference contacts, since only one resistor, R_2, remains in circuit when the pressure-arm contactor bears against one of these contacts, and, hence, a high reference modulating frequency is obtained. Contacts of the second group, comprising contacts numbers 5, 10, 20, 25, 35, 40, 50, 55, 65, 70, and 80, are termed the low reference contacts, R_2 and R_1 being in circuit when the contactor bears against one of these contacts and a somewhat lower reference modulating frequency being then obtained.

The sequence of switching operations serves as indication, by actual count, of the particular contact being reached by the pressure-arm contactor and, thus, from prior calibration, of the actual ambient pressure. This count is much facilitated by the occurrence of the high reference frequency every fifteenth contact and of the low reference frequency at intervening fifth contacts. In this usage, the reference frequencies serve as index points on the pressure scale. They are also useful in determining whether the balloon is ascending or descending.

To evaluate the temperature and humidity observations at the ground station, it is necessary to measure the received modulation frequencies and to interpret the measurements in terms of standard charts and scales which relate the frequency-resistance characteristics of the radio-sonde transmitter to the resistance-temperature characteristic of the temperature tube and the resistance-humidity characteristic of the electric hygrometer. The availability of the reference frequencies renders it practicable to carry out the measurements and evaluations in terms of the ratios (to either reference frequency) of the modulation frequencies produced when the measuring elements are in circuit. For convenience, the lower reference frequency is used as the control point, a nominal value of 190 cycles per second being employed for this reference.

By means of a proportional scale control in the frequency-measuring equipment at the receiving station, the lower reference frequency is made to read a predetermined nominal value regardless of its absolute value. The observed frequencies corresponding to the temperature and humidity connections are then seen to be measured in terms of the nominal reference frequency. As will be shown later, the ratio of the modulation frequencies corresponding to any two particular values of circuit resistance remains very nearly constant under all operating conditions. On this basis, it will be evident that the observed frequencies actually correspond to the values of the resistance in circuit referred to the value of the reference resistor (R_2+R_1). By keeping (R_2+R_1) constant within 0.5 percent and the shunt resistor (R_6) constant within 3 percent, it becomes possible to obtain very nearly the same relation between observed modulation frequency and circuit resistance for all radio-sonde transmitters, so that a standard frequency-resistance characteristic curve may be used in all soundings. Since the temperature tube and the electric hygrometer may also be produced to have practically identical variation of resistance with temperature and humidity, respectively, for all units produced, the measurement and evaluation of temperature and relative humidity become possible without requiring individual calibration of the component elements involved. This represents a material saving in the cost of the radio sonde.

The method of measuring relative rather than absolute modulation frequencies affords several additional operating advantages. The condenser, C_2, in the resistance-capacitance network need not be adjusted to secure the exact standard low reference frequency, since a variation of ± 10 percent can be taken care of readily by the proportional scale control in the frequency-measuring circuit. Moreover, reference-frequency drift in the radio-sonde transmitter, produced by variations in tube parameters due to varying battery voltages and by temperature effect on the condenser, C_2, can be handled similarly. Finally, the standard frequency-resistance characteristic may be modified at individual receiving stations to include small calibration corrections for the frequency-measuring equipment. The significance of these factors in reducing required manufacturing tolerances (and hence cost) is self-evident. The only assumptions made in following the procedure are that the frequency scale in the measuring equipment is substantially linear (within 1 percent) and that the resistors (R_2+R_1) and (R_6) in the radio-sonde transmitter may be held to within 1 and 6 percent, respectively, under the ambient-

temperature conditions encountered during operation. These conditions are readily fulfilled.

2. CONSTRUCTIONAL DETAILS OF RADIO SONDE

Details of the radio sonde are shown in figures 4, 5, and 6. The temperature tube and electric hygrometer are fastened to opposite sides of a mounting plate which fits into the inner of two thin concentric aluminum tubes (see *e* in fig. 6). These form the radiation shields for protecting the temperature and humidity elements from heating by solar radiation. The container shown in figure 6 comprises a light cardboard case covered with a metallic foil. The front compartment houses the radio transmitter (*a*), the plug-in battery power supply (*b*), the pressure-switching unit (*c*), and the miniature relay (*d*). The rear compartment supports the radiation shield (*e*). The shield normally extends about two centimeters above its compartment and the top edge of the mounting plate is normally flush with the top edge of the shield. The temperature and humidity elements are ventilated by the flow of air through this shield produced by the upward movement of the balloon.

An important feature of the instrument is the thermal insulation provided for the radio-sonde transmitter and battery coupled with the thermal isolation of the temperature and humidity elements from the main radio-sonde assembly. There are two contradictory requirements in the design of a radio sonde: the radio transmitter and battery unit should be kept at as nearly constant temperature as possible in order to maintain stability of operation and conserve battery capacity, whereas the temperature- and humidity-sensitive elements should follow every variation of the ambient temperature. The first requirement is partially met by placing the transmitter and battery in a subcompartment formed by insulating material 1 centimeter thick (not shown in fig. 6). The requirement for complete thermal isolation of the temperature and humidity elements is readily carried out because only an electric connection of these elements to the remainder of the assembly is required. Data on the effectiveness of these features will be given later in this paper.

The complete instrument weighs slightly less than 1 kilogram and its present unit price in quantities of several thousand is about $25.00. An interesting feature of the instrument is that, with the radiation shield assembly slid down into its cardboard container, top and bottom flaps (tied back during the ascent) may be used for closing off this container. The instrument is then in convenient form for shipping or for return through the mail upon its recovery. Complete mailing instructions and the reward offered for its return are printed on the foil cover.

3. GROUND-STATION EQUIPMENT

Typical ground-station receiving and recording equipment are shown in figure 7. The receiving set (*a*) feeds an electronic frequency meter (*b*) which measures the frequency of the modulating signal from the balloon and converts it into a direct current proportional to the frequency. This is indicated by a microammeter on the electronic frequency meter and is simultaneously recorded by a recording microammeter (*c*).

An important operating feature of the electronic frequency meter is that the current is directly proportional to the frequency within

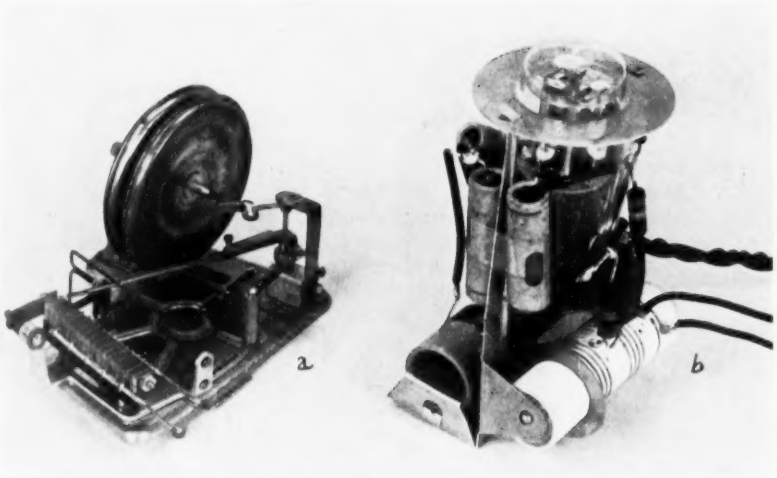

FIGURE 4.—*Component elements of radio sonde.*

a, pressure-switching element; *b*, radio-sonde transmitter.

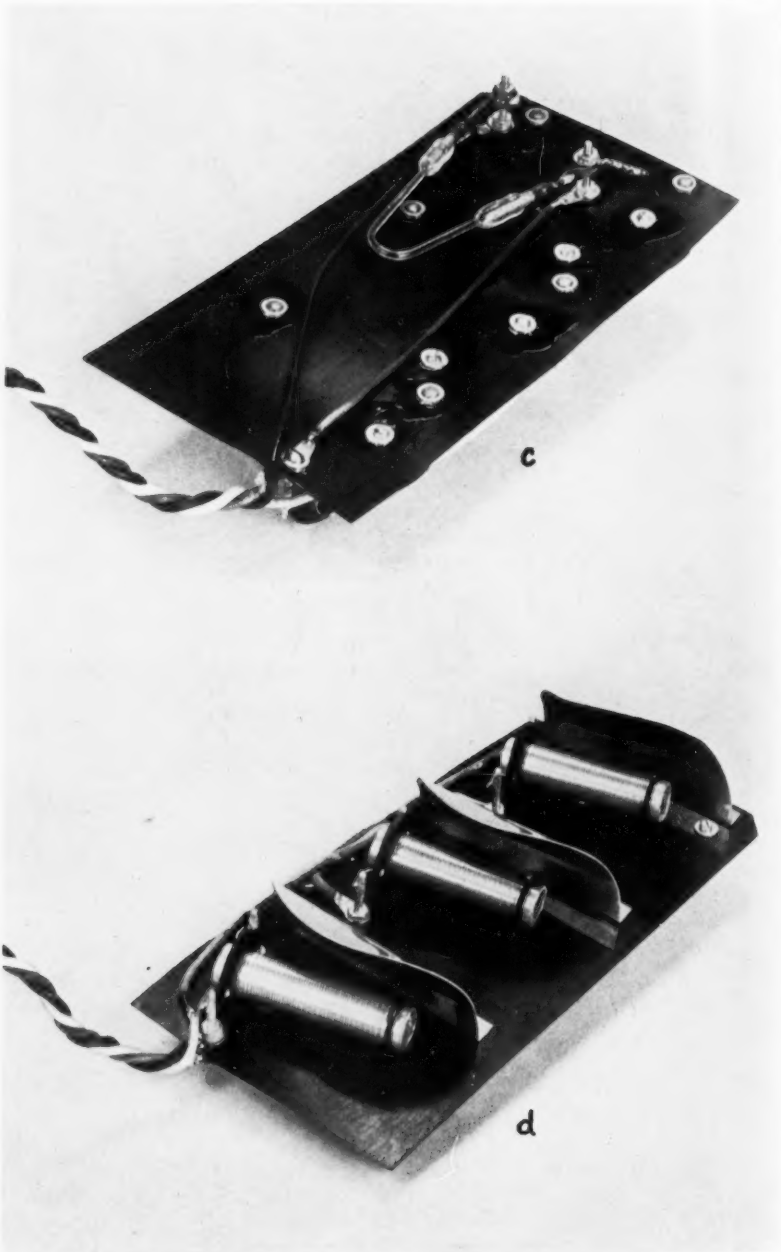

FIGURE 5.—*Component elements of radio sonde.*

c, temperature element; *d*, electric hygrometer.

FIGURE 6.—*Radio-sonde component elements in their container.*

a, radio-transmitter; *b*, battery power supply; *c*, pressure-switching unit; *d*, miniature relay; *e*, radiation shields; *f*, temperature tube; *g*, electric hygrometer.

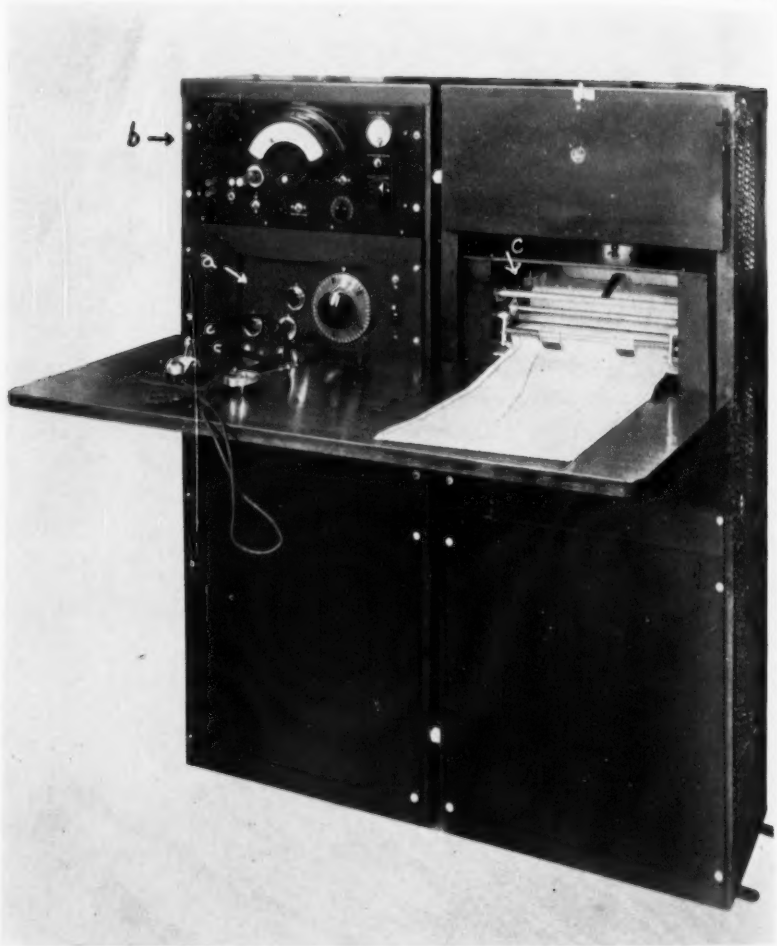

FIGURE 7.—*Ground-station receiving and recording equipment.*

a, receiving set; *b*, electronic-frequency meter; *c*, recording microammeter.

very narrow limits. Moreover, a control in the output circuit allows adjustments of the current corresponding to any frequency within the range, up to ± 15 percent, without upsetting the linear relationship between the current and frequency throughout the range. The use made of this property in the temperature and humidity measurements has already been explained.

4. RECORD OF A TYPICAL SOUNDING

A record of a typical sounding, redrawn for reproduction, is shown in figure 8. The start of the record, corresponding to the release of the balloon, is at the bottom of the chart. The recorder chart has 100 equally spaced divisions corresponding to a full-scale range of 200 cycles per second; however, it is more convenient for station personnel to work in terms of the recorder divisions, which may be considered as arbitrary frequency units. For an approximate interpretation of the record, a scale of temperatures (for an average temperature tube) and scales of humidities (at two ambient temperatures) are marked on the chart.

The traces at the extreme right of the chart represent the high-reference frequencies, while the traces just to the left of these represent the low-reference frequencies. The physical positions of the pressure-arm contactor as these marks were being traced by the recorder may be visualized by referring to the contact numbers shown at the lower edges of the high-reference traces. (See also figs. 3 and 4.) The altitude of the balloon corresponding to each high-reference trace is marked on the chart as of likely interest to the reader. Altitude is determined by the well-known hypsometric formula, using the pressure, temperature, and humidity observations.

The temperature and humidity traces are seen to form broken lines which plot the variation of these two meteorological factors as a function of the balloon altitude. The temperature traces are readily distinguishable from the humidity traces by the nature of their variation. Each interruption of the temperature plot designates that the pressure-arm contactor has just reached a humidity or reference contact; each interruption of the humidity plot indicates that the contactor has just left a humidity contact. Light dotted lines have been added between adjacent humidity traces to emphasize the sharp variations obtained.

5. EVALUATION CHARTS

Special charts are employed for facilitating the evaluation of pressure, temperature, and humidity from the recorded observations. Since the pressure-switching units are individually calibrated, the evaluation of pressure is made directly from the calibration chart.

One arrangement for evaluating temperature employs a special slide rule. The fixed scale is graduated in recorder divisions, spaced to represent, on an arbitrary logarithmic scale of resistance, the standard frequency-resistance characteristic of the radio-sonde transmitter. The sliding scale is graduated in temperature divisions which plot the temperature-resistance characteristic to the same arbitrary logarithmic scale of resistance. In this way, adjustment of the sliding scale with respect to the fixed scale provides for automatic correlation of the transmitter characteristic with the temperature-tube characteristic. It allows the actual value of resistance of the temperature tube at a given temperature to vary within rather

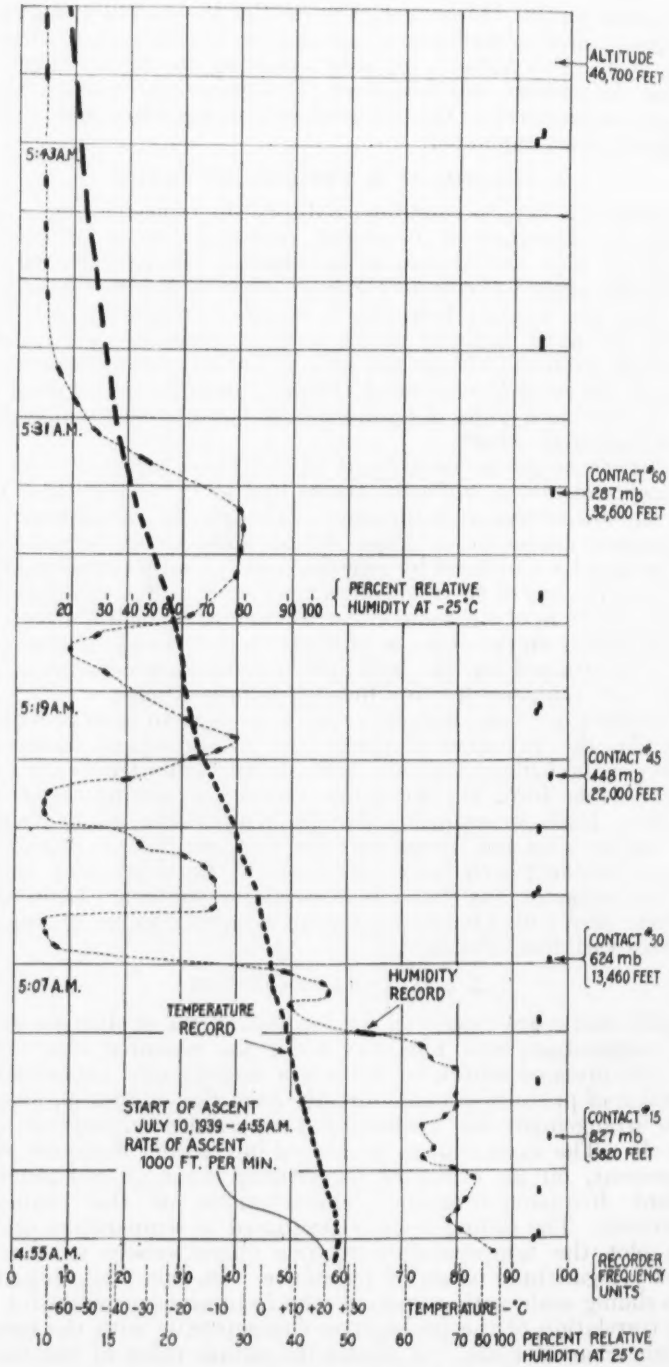

FIGURE 8.—*Record of a typical sounding.*

wide limits (thereby reducing the accuracy to which the bore of the tube must be held in manufacture), so long as its law of variation of resistance with temperature corresponds to the standard electrolyte used.

Just prior to the release of the radio sonde, the operator measures the true temperature at the ground surface and the corresponding observed trace on the recorder. These data are used in setting up the slide rule. Evaluation of observed temperatures from observed recorder traces during the sounding are then carried out by means of the cruiser on the slide rule.

The chart used for evaluating the humidity observations is shown in figure 9. It facilitates the application of a temperature correction

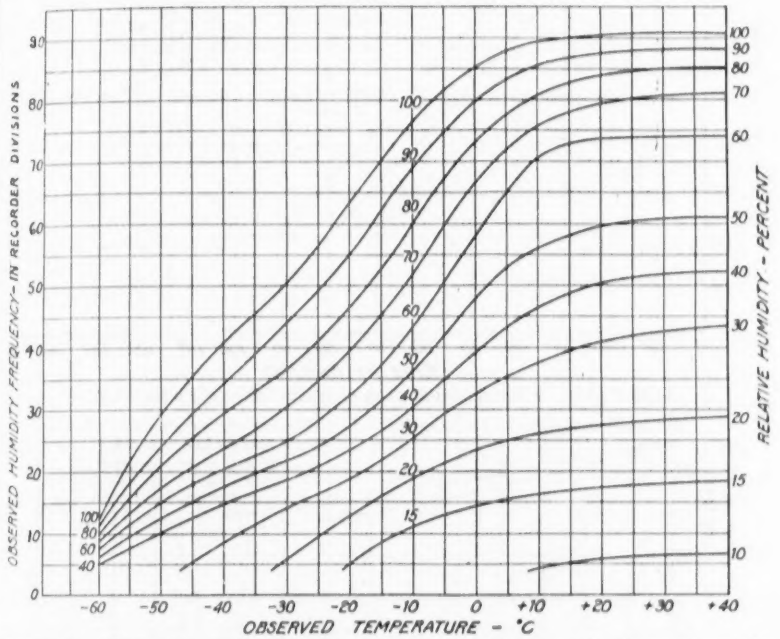

FIGURE 9.—*Charts for evaluating the relative humidity from the observed recorder frequency and the temperature at which the observation is made.*

to the humidity readings. The ordinate scale is in arbitrary frequency units corresponding to divisions on the recorder chart. The scale of abscissas represents the temperature at which the humidity measurements are made. Each curve is for a constant relative humidity. Knowing the frequency of the observed humidity trace and the corresponding observed ambient temperature, the relative humidity is determined by interpolation on the chart. Reasonable control of the manufacturing processes makes it possible to obtain electric hygrometers which conform very closely to the standard characteristics of figure 9.

IV. PERFORMANCE OF COMPONENT ELEMENTS

The following sections will present the results of numerous tests on component elements of the radio sonde under idealized conditions in the laboratory and under actual field conditions.

1. RADIO-SONDE TRANSMITTER

The radio-sonde transmitter operates under conditions which can hardly be considered conducive to stable operation. The change of

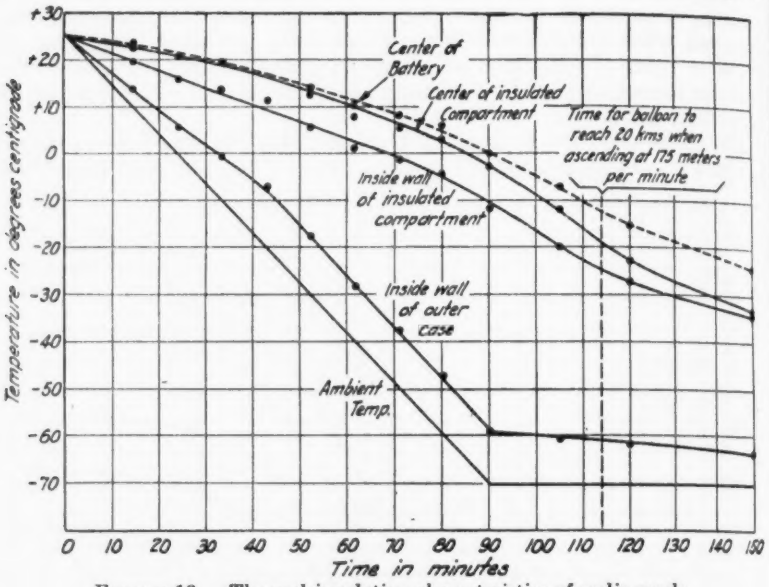

FIGURE 10.—*Thermal-insulation characteristics of radio sonde.*

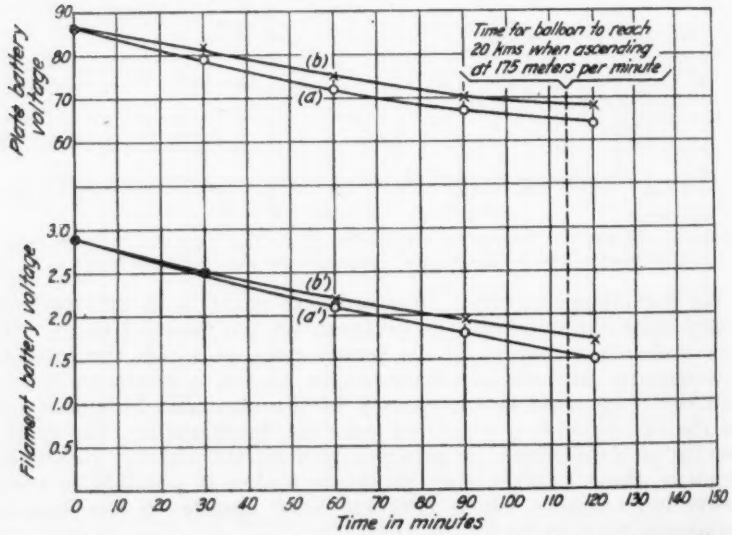

FIGURE 11.—*Variation of battery voltages with time during a radio sounding.*

ambient temperature within the radio-sonde case, during the course of a sounding, may exceed 100 degrees centigrade; the plate and filament battery voltages may decrease to 65 percent of their rated values. The important considerations in performance are: the fre-

quency stability of the carrier oscillator, the variation of carrier power output with time, and the degree of maintenance of the audio-frequency (frequency-resistance) characteristic.

Figure 10 shows the variation of the temperature at selected points in the radio sonde when the ambient temperature variation and ventilation simulate those encountered during a typical radio sounding in the summer (when maximum ambient-temperature change occurs). The ambient-temperature change assumed corresponds to a balloon ascension rate of 175 meters per minute. On this basis, the balloon reaches 20 kilometers in 114 minutes. The temperature in the insulated compartment housing the transmitter and battery is then seen to be about −20° C. With the increased rate of ascent made possible with the improved instrument, say 300 meters per minute, the corresponding temperature at 20 kilometers would be approximately zero degrees centigrade. In either case, the insulated compartment is seen to afford considerable protection for the radio transmitter against the ambient-temperature change.

Figure 11 shows the variation in terminal plate and filament voltages as the radio sonde ascends at 175 meters per minute through a standard atmosphere. Graphs *a* and *a′* are for the radio sonde as used heretofore, without the insulated subcompartment. Graphs *b* and *b′* are for the radio sonde, using the insulated subcompartment. There is seen to be a material increase in the time to reach given terminal voltages when using the insulation.

(a) FREQUENCY STABILITY AND POWER OUTPUT OF CARRIER OSCILLATOR

Figure 12 shows the variation in carrier-oscillator frequency as a function of the various operating parameters. Graph *a* shows the variation with the temperature of the oscillator compartment. Graph *b* shows the variation with filament voltage; graph *c*, the variation with plate voltage; and graph *d*, the variation with time when both voltages vary as shown by graphs *b* and *b′* in figure 11. The variation of the carrier-oscillator frequency with antenna tuning is shown by graph *e;* since the antenna tuning remains substantially constant, very little of the variation shown in graph *e* actually occurs.

A study of figure 12 in combination with figures 10 and 11 indicates that the over-all carrier-frequency variation occurring during a sounding probably does not exceed 100 kilocycles per second. It would appear possible to reduce this variation to the order of 40 kilocycles per second through the addition of a tuning condenser having a negative temperature coefficient.

The power radiated from the dipole transmitting antenna averages 200 milliwatts at rated plate and filament voltages. At the end of 2 hours' operation under the average conditions encountered during a sounding, the average radiated power drops to about 75 milliwatts.

It is of interest to consider briefly the receiving problem at ground stations arising from the limited transmitter output. The problem is complicated by the fact that it is desirable to eliminate nulls in the vertical receiving response pattern, since the balloon elevation angles may be from 80 degrees at the beginning of an ascent to 5 degrees or less at the end. Nulls are eliminated by placing the receiving antenna at one-half wavelength or less above ground. This results in very low response at balloon distances of the order of 100 to 200 kilometers.

Thus, with the balloon at 20 kilometers altitude and 150 kilometers distance, the field intensity set up at the receiving antenna (for 100 milliwatts output) is only 12 microvolts per meter.

An effective expedient to increase the distance range of reception

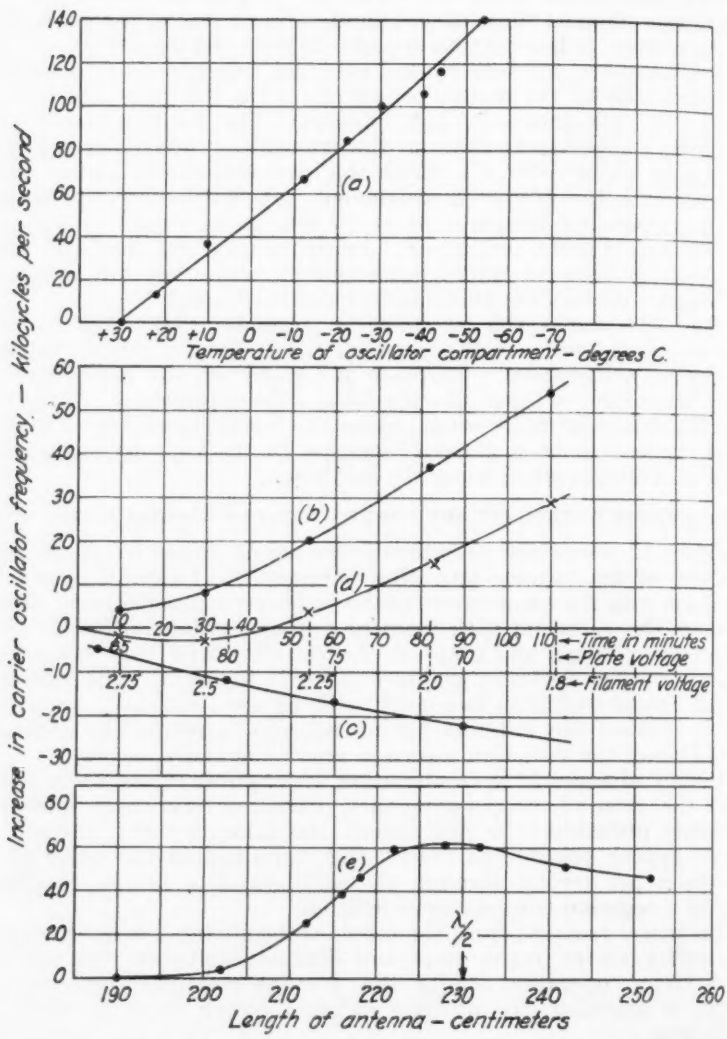
Increase in carrier oscillator frequency — kilocycles per second
(a)
+30 +20 +10 0 -10 -20 -30 -40 -50 -60 -70
Temperature of oscillator compartment — degrees C.
(b)
(d)
(c)
10 20 30 40 50 60 70 80 90 100 110 ← Time in minutes
85 80 75 70 ← Plate voltage
2.75 2.5 2.25 2.0 1.8 ← Filament voltage
(e)
λ/2
190 200 210 220 230 240 250 260
Length of antenna — centimeters

FIGURE 12.—*Graphs showing frequency variation of 65–Mc carrier oscillator.*

a, With temperature of oscillator compartment; *b*, with filament-battery voltage; *c*, with plate-battery voltage; *d*, with both voltages; *e*, with antenna length.

is to employ a second antenna placed one and one-fourth wavelength above ground and put into operation only when reception on the first antenna proves difficult. The vertical receiving response patterns for the two antennas are shown in figure 13; they are seen to intersect at 17 degrees. For the distance and height of balloon con-

sidered, the field intensity at the second antenna is approximately 18 microvolts per meter, an appreciable improvement. It will be evident that the improvement will be even greater at lower elevation angles or when the dielectric constant of the ground is lower than the assumed value of 15.

(b) MAINTENANCE OF AUDIO-FREQUENCY CHARACTERISTIC

As previously indicated, the radio-sonde transmitters are readily controlled to conform to a standard audio-frequency characteristic. This characteristic is shown by the solid curve in figure 14. The

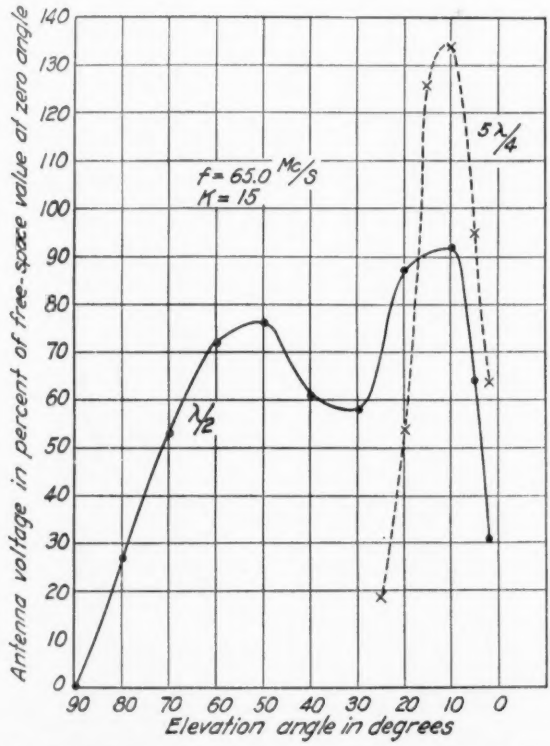

FIGURE 13.—*Vertical-plane directivity of receiving antennas at ground station.*

dotted curves on either side of the solid curve represent characteristics having the maximum deviation from the standard in 100 stock transmitters tested. It is to be noted, particularly, that whenever a deviation from the standard characteristic is noted, all points of the characteristic obtained lie on the same side of the standard curve. The characteristics for the transmitters tested were determined on the basis that the low-reference frequencies were all equal to 190 cycles per second; actual variations in the reference frequency ranged from +10 to −15 cycles. Thus, the abscissas in figure 14 represent indicated frequencies corrected for a reference frequency of 190 cycles per second; the ordinates correspond to values of resistance added in series with (R_1+R_2) of figure 3.

During a sounding, the absolute value of the reference frequency will be affected by variations in several of the operating parameters. These include the plate and filament voltages of the modulating oscillator, the condenser C_2 in the resistance-capacitance network, and the series resistance of the oscillatory circuit $L_1C_1L_2$. (See fig. 3.)

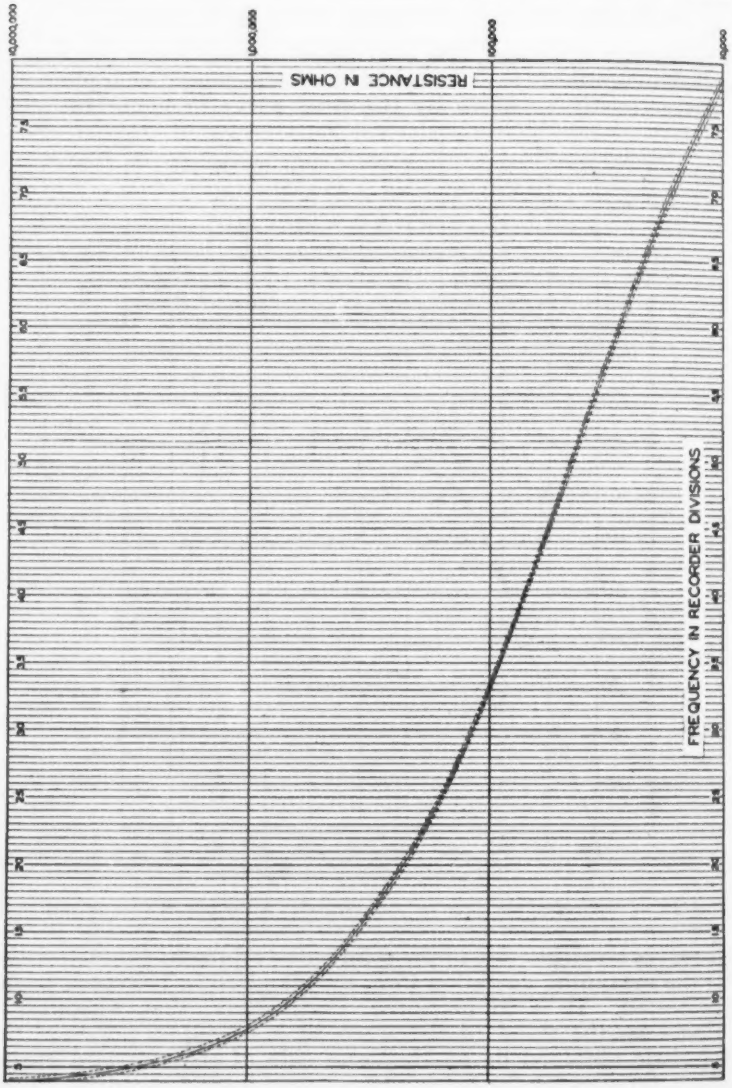

FIGURE 14.—*Range of variation of transmitter audio-frequency characteristic.*

The effect of battery-voltage change is shown in figure 15, graph *a*; here the abscissas represent the simultaneous variation of the plate and filament battery voltage during a sounding. The influence of the battery voltages upon the value of the "blocking" frequency is due to the attendant change in the transconductance of the tube, which

affects the amplitude of the 1-megacycle oscillations and also the values of grid bias at which these oscillations begin and stop. As the battery voltages decrease in value, the amplitude of oscillation decreases, thereby increasing the time for charging the condenser C_2 of figure 3. Since the discharge time for this condenser depends only on the value of C_2 and of the resistance in parallel with it, the

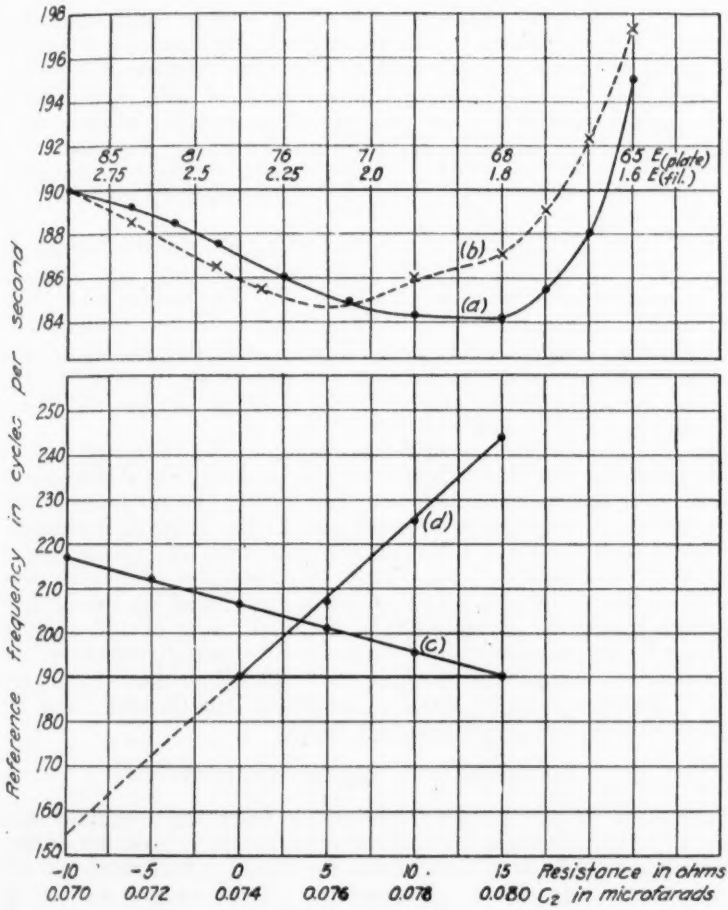

FIGURE 15.—*Graphs showing drift of low-reference frequency of modulating oscillator.*

a, with battery voltage change; *b*, with battery voltage change under operating conditions; *c*, with value of condenser C_2 (fig. 3); *d*, with resistance of oscillatory circuit $L_1C_1L_1$ (fig. 3).

total time per period varies with the amplitude of oscillation, increasing as the amplitude of oscillation decreases. Thus, there is a tendency for the blocking frequency to drop as the voltages decrease.

However, as the voltages decrease, the limits of grid bias between which oscillations are maintained vary, the extent of such variation

depending upon the shape of the plate current-grid voltage characteristic of the triode. The variation due to this effect is initially quite small but becomes appreciable when the battery voltages approach about 60 percent of their rated values; the tendency is to produce an increase in the blocking frequency. The influence of the tuning condenser, C_1, is similar to this effect in that it controls the effective series resistance of the tuned circuit and, hence, the portion of the tube characteristic along which oscillations occur. Changes of ± 15 percent in the value of C_1, for example, due to temperature, have negligible effect on the blocking frequency.

Graph *b* of figure 15 shows the variation of reference frequency under actual operating conditions during a sounding plotted against the same scale of abscissas as graph *a*. From the similarity of the two graphs, it will be evident that the added effects of changes in the values of C_2 and of the resistance in the oscillatory circuit ($L_1C_1L_2$) are quite small.

The effects of changes in the value of C_2 and in the resistance of the oscillatory circuit, on the blocking frequency, are shown by graphs *c* and *d*, respectively, of figure 15. The values of C_2 and of the effective circuit resistance both decrease with decreasing ambient temperature. Hence, during an ascent, the two effects tend to counterbalance. This accounts for the similarity of graphs *a* and *b* of figure 15; the former shows only the effect of the battery voltages whereas the latter includes all the effects.

The foregoing treatment of the variation of the reference frequency under operating conditions is introduced to show that it should apply equally well to other frequencies. Practically the only phenomenon whose effect is not exactly proportional to the blocking frequency is caused by the change in tube transconductance, and the deviation is small even in this case. Hence, since the frequency-resistance characteristic of the radio-sonde transmitter is considered on the basis of a reference frequency corrected to a nominal value of 190 cycles per second, the characteristic should remain substantially constant under the operating conditions encountered. This has been found to be true in practice, the maximum deviation encountered in a large number of tests being less than ± 1 cycle.

(c) ACCURACY OF THE MEASURING SYSTEM

The effect of the possible deviations from the standard audio-frequency characteristic which may arise in stock radio-sonde transmitters will now be considered from the viewpoint of resultant errors in the measurement of temperature. Temperature rather than humidity measurements will be treated, since the accuracy requirements for the former impose a greater task on the measuring system. A temperature tube of negligible error will be taken so that the errors obtained may be attributed in entirety to the measuring system. This is generally the case in practice. To make the discussion complete, errors arising from the frequency-measuring and recording equipment will also be considered. In order to show clearly the effects treated, errors of reading and of adjustment of the reference frequency (which may introduce temperature errors up to ± 0.2 degree) will be taken as negligible.

Table 2 summarizes the effect of variation of individual transmitters from the standard audio-frequency characteristic. The dotted char-

acteristics of figure 14, corresponding to maximum deviations encountered in practice, are considered. Were it not for the process of setting up the temperature-evaluation slide rule on the basis of the surface-temperature observation (conveniently referred to as the "temperature lock") the errors listed in column 2 of table 2 would be had. However, the "temperature lock" corresponds to a parallel lateral shift of the individual characteristic so that it intersects the standard characteristic at the observed frequency (generally in the range from 50 to 70 recorder divisions at surface temperatures). This one-point lock reduces the errors obtained to those shown in column 3 of table 2.

TABLE 2.—*Effect of maximum tolerances in transmitter characteristic*

[±1 cycle at 120 cycles per sec; ±½ cycle at 10 cycles per sec]

True temperature	Apparent error [1] in absence of ground temperature lock	Actual error
°C	°C	°C
+30	±1.9	0.0
+15	±1.4	.0
0	±1.1	±.1
−15	±.9	±.1
−30	±.8	±.1
−45	±.7	±.1
−60	±.7	±.2
−70	±.8	±.3

[1] Errors of successive readings have same sign except when transmitter characteristic crosses the standard characteristic. No case of such crossing of the characteristic has been observed in practice.

Table 3 summarizes the effect of reference-frequency drift occurring during a sounding. The drift assumed corresponds to that normally encountered in service. Column 3 of table 3 suggests large errors, provided corrections for reference-frequency drift are *not* applied. Such corrections may be made automatically by adjusting the proportional scale control in the frequency-measuring circuit so that the recorder trace corresponding to each received low reference frequency reads exactly 95 divisions, or the corrections may be applied to the temperature observations on a proportional basis. Theoretically, the application of the corrections should reduce the error discussed to zero, as indicated in column 4 of table 3. However, the reference-frequency drift may not be uniform between successive reference-frequency contacts. The last column of table 3 shows the possible errors arising in practice from likely variations in uniformity of drift.

TABLE 3.—*Effect of reference drift in transmitter*

True temperature	Average accumulated frequency drift	Apparent error without corrections for frequency drift	Actual error when corrections for drift are applied	Possible error due to nonuniform frequency drift between references
°C	c/s	°C	°C	°C
+15	0.0	0.0	0	0.0
0	.6	.9	0	.2
−15	1.2	1.1	0	.1
−30	1.9	1.2	0	.1
−45	2.7	1.2	0	.1
−55	3.6	1.3	0	.1
−55	5.0	1.7	0	.1

Table 4 shows the effect of using uncalibrated ground-station frequency-measuring and recording equipment. Calibrations made of a number of ground-station equipments yielded maximum deviations of the recorded traces from true frequency as indicated in figure 16. If this unit were used without calibration, the errors which would at first glance appear to be obtained in the temperature measurements are shown in column 2 of table 4. Again, the "temperature lock" (see point *L* on fig. 16) operates to make a frequency correction at the highest observed temperature (surface temperature), so that the effective errors in frequency measurement during the sounding correspond to the deviations from the base line, *A*, in figure 16 instead of from the *X*-axis. The actual errors in temperature measurement with an

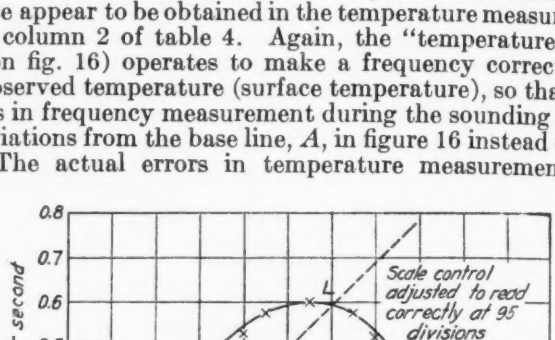

FIGURE 16.—*Effect of "temperature lock" in reducing errors caused by uncalibrated recorder.*

uncalibrated recorder thus reduce to the values shown in column 3 of table 4. These may of course be further reduced by calibrating the recorder equipment.

TABLE 4.—*Effect of errors in indication of frequency recorder*

True temperature	Apparent error for average recorder, uncalibrated	Actual error for average recorder, uncalibrated, with temperature lock as used	Actual error for calibrated recorder	True temperature	Apparent error for average recorder, uncalibrated	Actual error for average recorder, uncalibrated, with temperature lock as used	Actual error for calibrated recorder
°C	°C	°C	°C	°C	°C	°C	°C
+30	1.4	0.0	0	−30	0.3	0.2	0
+15	1.1	.0	0	−45	.2	.3	0
0	0.8	.1	0	−60	.2	.3	0
−15	.6	.1	0	−70	.2	.3	0

The foregoing analysis should serve to indicate that the application of corrections for reference-frequency drift coupled with the use of the "temperature lock" operate to provide an accuracy of temperature measurements which would not appear to be possible from a

casual analysis of the system. This conclusion is fully corroborated by actual performance, as will be shown later in this paper.

2. PRESSURE-SWITCHING ELEMENT

The measurement of pressure on the basis of contact identification considerably increases the practical accuracy of the pressure observations. Obviously, the limitation to accuracy lies only in the performance of the pressure diaphragm and pressure-arm linkage; no errors are introduced by the method of recording and evaluation. Tests on a large number of units revealed that readings are repeated to within the calibrating accuracy, less than 1 millibar. Since the temperature and humidity observations are generally taken at the contacts (where accurate calibration is available), the possible accuracy of the pressure measurements is seen to be within 1 millibar.

This accuracy is not attained in actual use because of the temperature coefficient of the diaphragm and because of zero shift during shipment and storage. The temperature effect is maximum at ground-level pressure and decreases at lower pressure levels until nearly exact temperature compensation is had at about 150 millibars. Thus, if the calibration is carried out at room temperature, the reading at ground-level pressure may be in error by up to 10 millibars if the temperature of the diaphragm is, say, −40° C; however, the error at 150 millibars will be negligible. In service use it is customary to rely upon the temperature lag of the diaphragm to limit the temperature error at the higher pressure levels. Since the radiosonde container provides some thermal insulation of the pressure element, the error introduced is normally less than 3 millibars at usual winter surface temperatures. A more accurate procedure, under present consideration, is to apply temperature corrections to the pressure observations, based on the average behavior of a large number of pressure units. There remains also the possibility, avoided at present owing to its cost, of adding automatic compensation for the temperature error.

The zero shift operates to displace the calibration curve parallel to itself, so that all pressure readings are in error by very nearly the same amount. To correct for zero shift, a control is provided for moving the switching element laterally with respect to the pressure-arm contactor. This control allows setting the unit correctly at the ground-level pressure prior to an ascent, the adjustment being generally made at room temperature.

Some refinement in setting the control would result in increased accuracy over that now attained. The adjustment is at present made on the basis of visual observation of the position of the switching contactor on the surface of the switching element and may introduce an error up to 3 millibars. This, coupled with the residual error due to temperature effect, results in over-all error in practice up to 5 millibars. It is important to note that practically no scattering of readings occurs, the over-all error being of very nearly the same magnitude and of the same sign throughout the range of indication. Hence, the relative accuracy of successive pressure observations is generally within about 1 millibar.

During the design of the instrument, some difficulty was expected in practice from corrosive action on the contacts. Fortunately, such

difficulty has not materialized. It is customary to clean the surface of the switching element with very fine abrasive paper just prior to use. This procedure appears to have solved the problem of securing good contacts even at locations such as Swan Island in the Caribbean and ship stations in the Atlantic and Pacific.

3. TEMPERATURE ELEMENT

A description of improvements effected in the electrical properties of the temperature element is given elsewhere [4]. With the development of a practical seal for the terminals, the useful life of the device has been increased to about a year. Comparative tests of units 1 month and 8 months old showed agreement within the accuracy of measurement, ± 0.2 degree centigrade. During several years of use of the temperature tube, the same electrolyte formula has been used and all temperature tubes have been found to give identical characteristics within the limits of measurement (± 0.2 degree centigrade).

(a) SENSITIVITY OF INDICATION

The sensitivity of indication obtained may be defined as the change in modulating frequency produced per degree change in temperature. For a given portion of the range of temperature indication, it obviously depends on the slopes of the frequency-resistance characteristic of the modulating oscillator and of the resistance-temperature characteristic of the temperature element. The former has greatest slope for low values of resistance while the latter has least slope for low values of resistance (that is, high temperatures). Two factors allow some leeway in adjustment of the two characteristics so as to obtain reasonably uniform sensitivity throughout the temperature range. One consists in shaping the audio-frequency characteristic so as to maximize its slope at the low-resistance end, by making (R_1+R_2) of figure 3 as low as considerations of stability will allow (40,000 ohms), and to reduce its slope at the high-resistance end by adding the 1-megohm shunt resistor (R_6). The second means for adjustment consists in varying the dimensions of the temperature tube so as to vary the tube resistance corresponding to a given temperature. Since the temperature coefficient of resistivity of the electrolyte used does not vary, this adjustment determines the portion of the audio-frequency characteristic utilized for a given portion of the temperature range.

The influence of the several possible adjustments on the sensitivity of temperature indication obtained may be seen from figures 17 to 19, inclusive. Figure 17 shows the effect of the value of series resistance used. Note that the sensitivity increases for the higher temperatures and decreases for the lower temperatures as the value of series resistance is reduced. The value chosen for use is 40,000 ohms. Figure 18 shows the effect of the shunt resistor. Note that only the lower temperatures are influenced appreciably. Above about 1 megohm, the slight advantage gained for sensitivity of indication of the lower temperatures is more than compensated for by the difficulty in receiving and measuring very low frequencies. A 1-megohm shunt is in present use. Figure 19 shows the influence of changing the resistance of the temperature tube. Increasing the tube resistance (correspond-

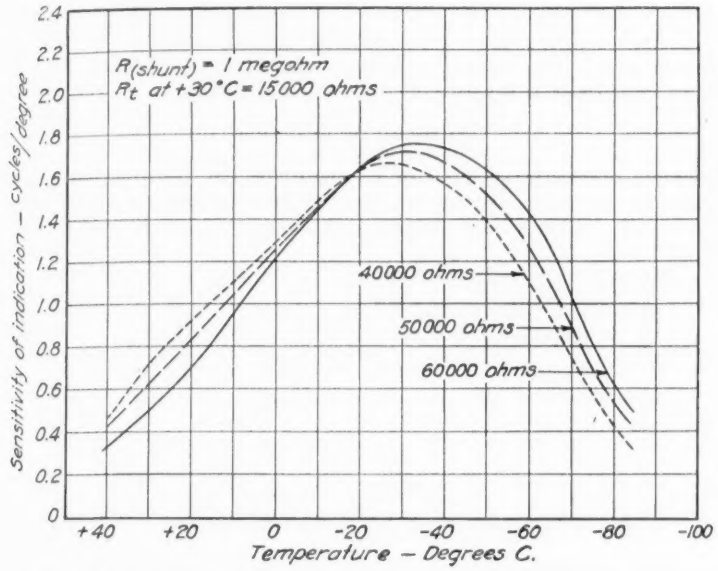

FIGURE 17.—*Effect of value of series resistor on sensitivity of temperature indication.*

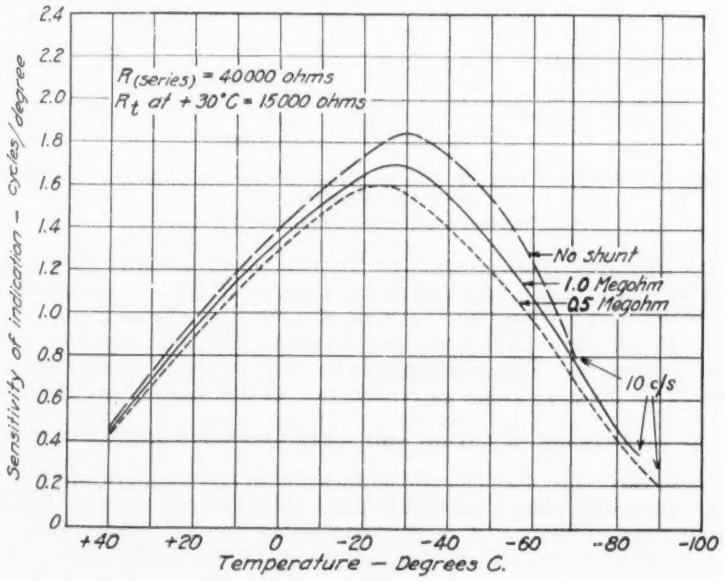

FIGURE 18.—*Effect of value of shunt resistor on sensitivity of temperature indication.*

ing to a given temperature, say +30° C.) improves the sensitivity at the higher temperatures but reduces the sensitivity for the lower temperatures. The value in present use, 15,000 ohms at +30° C, is seen to represent a reasonable over-all compromise.

(b) SPEED OF RESPONSE

Because of the large area of exposure of the temperature element relative to its mass, its response to ambient-temperature changes is quite rapid. This is an obvious advantage for radio-sonde service.

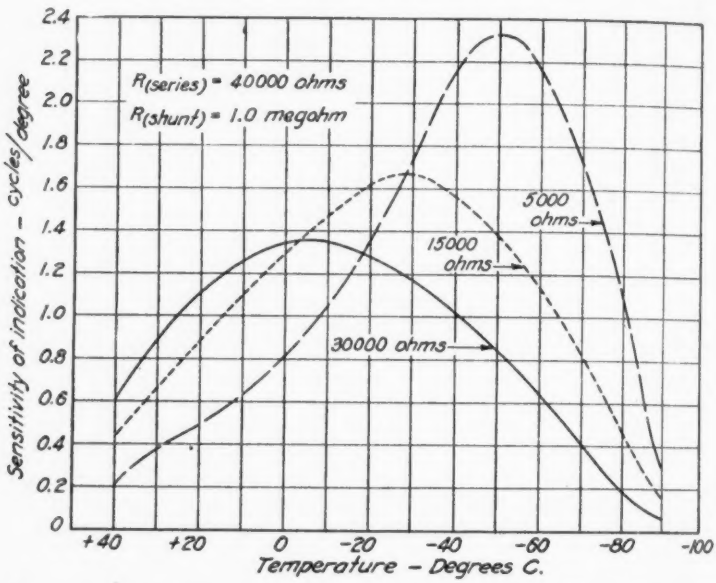

FIGURE 19.—*Effect of varying dimensions of temperature tube on sensitivity of temperature indication.*

Figures on graphs represent resistance at 30° C.

Figure 20 shows the variation of the time-lag constant [4] of the temperature element as a function of the velocity of the air passing it. It is evident that so long as the rate of ascent of the balloon exceeds about 150 meters (500 feet) per minute, the time-lag constant is about 8 seconds. This corresponds to only about 40 meters displacement of the balloon at an ascension rate of 300 meters per minute.

(c) THERMAL ISOLATION AND SOLAR-RADIATION SHIELDING

The advantages of an electric connection of the temperature element to the main radio-sonde assembly have already been noted. For true temperature indication it is important that the temperature element be isolated thermally from the remainder of the radio sonde. Also,

[4] The time-lag constant is the time required for the indication to show a change of $\left(1-\frac{1}{e}\right)$ of the total change, where e is base of natural logarithm [5].

to make daytime soundings possible, effective shielding against solar radiation is essential. The design shown in figure 6 was adopted after numerous ascension tests of a large number of case designs affording a variety of exposures of the sensitive elements. The temperature measurements obtained in the stratosphere testified to the importance of thermally isolating the temperature element from the remainder of the radio sonde. To serve as a standard of comparison, an assembly comprising two completely detached units (except for the connecting wires) was tried; in this arrangement the radiation-shield assembly was suspended about 18 inches above the main portion of the radio sonde. This arrangement was found to give the coldest temperatures in the stratosphere. The design shown in figure 6, although giving stratosphere temperature indications up to 1 degree warmer, was adopted because of the more convenient handling. The older design,

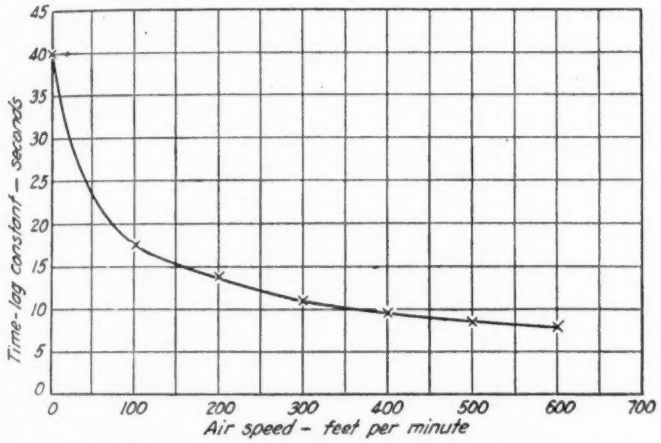

FIGURE 20.—*Variation of time-lag constant of temperature element as a function of ventilation.*

using a balsa-wood case, gave stratosphere temperature indications up to 2 degrees warmer. Other designs tested gave temperature indications up to 15 degrees warmer. Some of these were similar to designs used by other experimenters.

Sample results of the tests are shown in figure 21. Two instruments were attached to the same balloon, one having the case shown in figure 6 and the other having a round case made of balsa wood, with the sensitive elements mounted beneath the case and ventilated by eddy currents about the radiation shield. Two hours later a third instrument was released having a round case made of metal with the sensitive elements mounted beneath the case and similarly ventilated; to prevent heat conduction the radiation shield was thermally insulated from the metal case. It will be observed that the round-case instruments gave warmer temperature observations than the standard instrument, the divergence increasing as the altitude (and hence solar exposure) increased. A significant check is obtained at the point of bursting of the balloons. It will be noted that the temperature observations during the descent of the round-case

instruments check the ascending observations of the standard instrument. The added ventilation due to the greater speed of descent (1,500 feet per minute), coupled with the fact that the air stream reaching the sensitive elements has not been warmed by passing over the case (as in the ascent), accounts for the colder temperature obser-

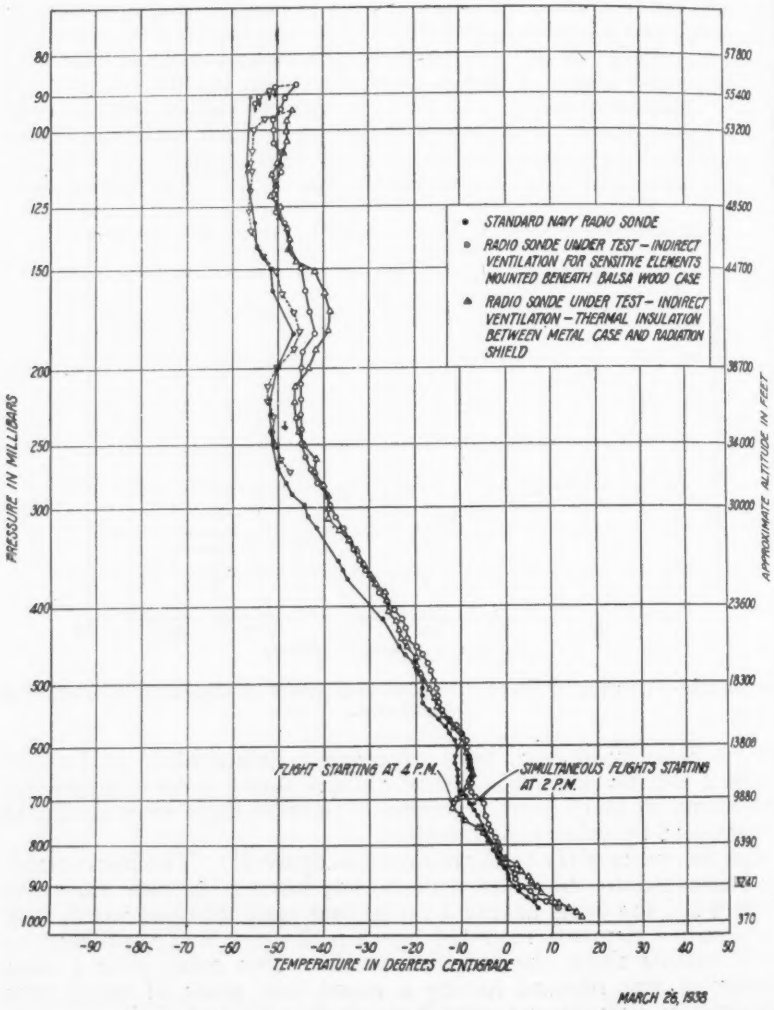
STANDARD NAVY RADIO SONDE
RADIO SONDE UNDER TEST – INDIRECT VENTILATION FOR SENSITIVE ELEMENTS MOUNTED BENEATH BALSA WOOD CASE
RADIO SONDE UNDER TEST – INDIRECT VENTILATION – THERMAL INSULATION BETWEEN METAL CASE AND RADIATION SHIELD
FLIGHT STARTING AT 4 P.M.
SIMULTANEOUS FLIGHTS STARTING AT 2 P.M.
PRESSURE IN MILLIBARS
APPROXIMATE ALTITUDE IN FEET
TEMPERATURE IN DEGREES CENTIGRADE
MARCH 26, 1938

FIG. 21.—*Comparative soundings with different radio-sonde case designs to evaluate degree of thermal isolation of temperature element*

vations during the descent. The agreement with the ascending observations of the standard instrument adds evidence that the latter are correct.

Further evidence on the effectiveness of the thermal isolation is given in figure 22. The data were obtained from a sounding with a

single instrument at noon on a September day. A special pressure-switching element [6] was used which gave accurate pressure measurements at 2-millibar intervals starting from about 145 millibars.

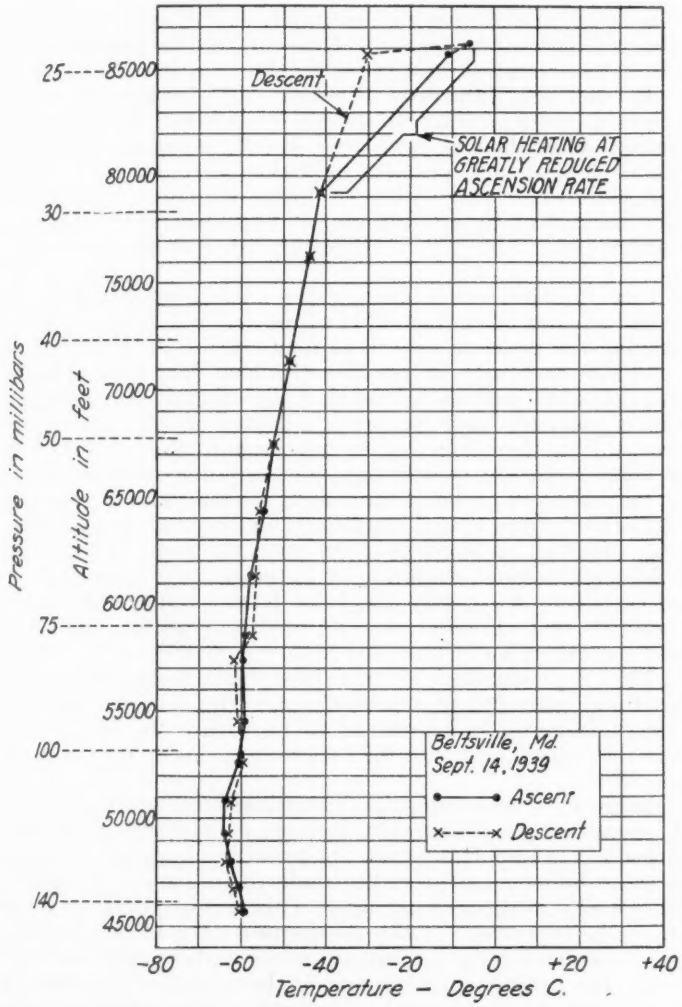

FIG. 22.—*Stratosphere sounding showing temperature observations during ascent and descent of balloon*

Measurements were obtained during both the ascent and descent of the balloon, the rate of ascent being 300 meters per minute and the rate of descent 500 meters per minute. At pressure levels below about 30 millibars, the balloons were obviously floating, so that the temperature element had insufficient ventilation. However, when the balloons broke, the temperature element soon assumed the ambient

temperature. Note the close agreement of the ascending and descending values under considerably different ventilating conditions.

(d) ACCURACY OF INDICATION

Two methods of evaluating the accuracy of the radio-sonde temperature observations are available. One consists in placing the radio sonde in a test chamber and reducing the temperature and pressure in the chamber simultaneously at a time rate simulating the changes which would occur during an actual sounding. The temperature observations may then be compared directly against standard thermometers. The second consists in making simultaneous soundings with the radio sonde and with a recording meteorograph (carried on the same balloon or by an airplane) and comparing the temperature observations from the two instruments at corresponding pressure levels.

The first method, often termed the "flight-similitude method", affords the obvious advantage of convenience in testing. The reason for changing the pressure as well as temperature in the test chamber is to simulate as nearly as possible the heat loss by conduction in various parts of the radio sonde so that the effect of temperature upon component elements may be truly reflected in the measurements. However, this method fails to take into account the influence of heating by solar radiation during daytime soundings and other factors such as variations in ambient humidity, ventilation, etc. Because of these departures from actual conditions and because of the ordinarily negligible effect of ambient pressure upon the temperature observations, the simultaneous variation of pressure may be omitted. The method is thereby materially simplified from a radio viewpoint, since a nonmetallic test chamber may be used and the loading effects of metal on the antenna circuit of the radio sonde eliminated. Approximately 100 "flight-similitude" tests have been made, using both the simplified and more complex procedures. The accuracy of temperature observations obtained proved to be within the limits specified earlier in this paper, that is, ± 0.75 degree centigrade for temperatures above $-50°C$.

The second method assures the determination of performance under actual operating conditions but introduces a number of practical difficulties. It is important that the recording instrument be carried by the same balloon as the radio sonde to insure direct comparison to heights well into the stratosphere. This requires that the recording instrument be recovered for the comparison data to be available. A practical expedient is to use simultaneous radio-sonde and airplane soundings; the recording instrument is then available as soon as the airplane returns to the ground. However, the airplane cannot generally fly in the same portion of the air mass as the balloon and its ceiling height is limited.

A large number of comparison tests of this general class have been made, including approximately 30 simultaneous radio-sonde and balloon-meteorograph soundings for which the meteorographs were recovered and about 150 simultaneous radio-sonde and airplane soundings. The majority of these tests were made in the field, using stock radio sondes with no special handling. The results of 20 simultaneous soundings of the first type are summarized in graph 1 of

figure 23, and the results of 25 of the second type in graph 2. The abscissas represent deviations between the radio-sonde observations and the observations of the comparison instrument, while the ordinates represent the percentages of the total observations falling within the specified deviations. In graph 1 temperature comparisons down to about −50° C are included, whereas in graph 2 the comparisons include data only down to −30° C. In considering the results, it should be noted that the deviations include the effect of errors in the comparison instrument as well as in the radio sondes. Also, since the pressure measurements with the two types of instruments were required in computing altitude in order that the temperature observations might be compared at equivalent altitudes, the deviations include the effect of possible errors in the observations of pressure.

The better agreement shown by graph 1 is attributed to the more direct comparison afforded when the two instruments are carried by the same balloon and hence traverse the same path through the atmosphere. In simultaneous radio-sonde and airplane soundings it is possible for the balloon to be as much as 75 kilometers from the airplane at the upper levels. To check the foregoing conclusion, a series of comparisons was made of simultaneous soundings with a radio sonde, a balloon meteorograph, and an airplane meteorograph (aerograph). The results of several of these are shown in the second paper of reference [2] and illustrate the better agreement between the two balloon instruments.

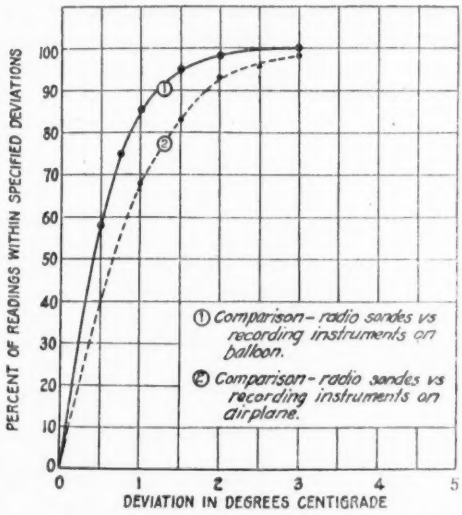

FIGURE 23.—*Summary of flight performance of temperature element.*

Using graph 1 of figure 23 as the basis for evaluating the accuracy of the radio-sonde temperature observations with the foregoing considerations in mind, it is evident that the specified accuracy of ±0.75 degree centigrade is undoubtedly attained in actual use.

4. ELECTRIC HYGROMETER

Details of the design of the electric hygrometer in its present form are given elsewhere [3]. Among the recent improvements are means for overcoming (a) the change of calibration of the device with time, (b) the presence of polarization effects, and (c) the lack of linearity of indication over the range of relative humidity measured. These improvements are described in the paper referred to; however, a few more words will be given here on the sensitivity of indication and speed of response. The accuracy of indication of the electric hygrometer will then be discussed.

(a) SENSITIVITY OF INDICATION

By using three elements (see fig. 5) coated with different lithium chloride solutions and interconnected with predetermined fading resistors, it is possible to provide for substantially constant sensitivity of indication throughout the humidity range corresponding to any desired ambient temperature. The combination in present use (see the calibration of fig. 9) was designed to provide practically constant sensitivity of indication at 0° C. The variation of sensitivity with humidity at this and other temperatures is indicated in figure 24.

It is important to note that the calibration of figure 9 is approximate for temperatures below about −15° C. Considerable difficulty is experienced in controlling and measuring relative humidity at temperatures below this value. The graph corresponding to 100-percent relative humidity is the only one which represents reasonably

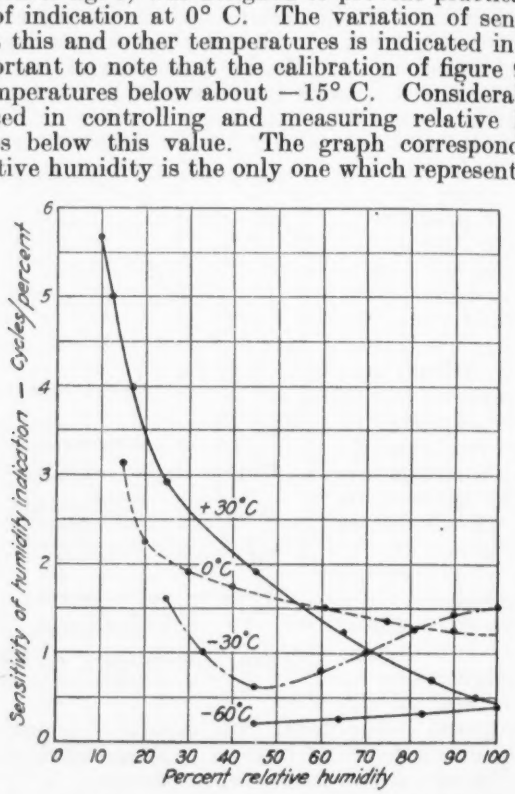

FIGURE 24.—*Sensitivity of indication of electric hygrometer.*

reliable data down to −60° C. It was obtained by placing the electric hygrometer in an ice enclosure and reducing the temperature of the whole mass by means of solid carbon dioxide. In this way it was found possible to maintain saturation within the enclosure, as witnessed by the fact that identical readings were obtained for decreasing and increasing temperatures. Further corroboration is afforded by the fact that this graph coincides with the locus of maximum recorded humidity frequencies at various low temperatures obtained in some hundreds of radio soundings. The difficulty in obtaining a reliable calibration of the electric hygrometer at low temperatures may perhaps be considered a disadvantageous aspect of the device. However, careful control in the manufacture of the device has resulted in substantially uniform characteristics, so that a calibration, once obtained, applies to all hygrometers.

(b) SPEED OF RESPONSE

The electric hygrometer has important advantages over other forms of hygrometers, particularly for radio-sonde application. In an earlier form of the radio sonde, still in use at about three-fourths of the stations of figure 1, a variable resistor controlled by the more conventional hair hygrometer is used for measuring relative humidity. Although useful observations are obtained, there are two limitations to this type. The first is that the hair hygrometer does not function effectively at temperatures below about 0° C; the second, that even at higher temperatures it does not respond sufficiently to the sharp changes in humidity encountered by a balloon ascending at the lowest practical rate (175 meters per minute). The electric hygrometer overcomes both of these defects. It is characterized by a rapid response to humidity variations at temperatures down to −60° C. Its rate of response is sufficient to permit any practical balloon ascension rate, as has been determined in actual tests at ascension rates of up to 400 meters per minute.

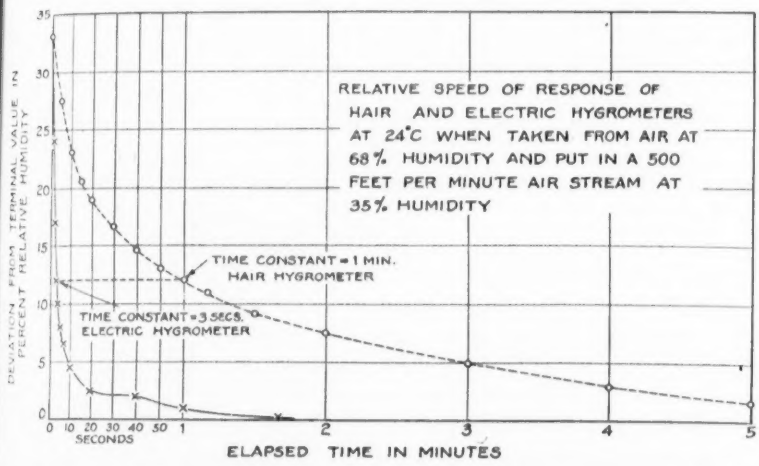
RELATIVE SPEED OF RESPONSE OF HAIR AND ELECTRIC HYGROMETERS AT 24°C WHEN TAKEN FROM AIR AT 68% HUMIDITY AND PUT IN A 500 FEET PER MINUTE AIR STREAM AT 35% HUMIDITY
TIME CONSTANT = 1 MIN. HAIR HYGROMETER
TIME CONSTANT = 3 SECS. ELECTRIC HYGROMETER
DEVIATION FROM TERMINAL VALUE IN PERCENT RELATIVE HUMIDITY
0 10 20 30 40 50 1 2 3 4 5
SECONDS
ELAPSED TIME IN MINUTES

FIGURE 25.—*Relative speeds of response of hair and electric hygrometers at 24° C.*

The much greater speed of response afforded by the electric hygrometer over the hair hygrometer will be evident from figures 25 and 26. The data of figure 25, taken at room temperature, show a time-lag constant for the electric hygrometer of only 3 seconds compared with 60 seconds for the hair hygrometer. The data of figure 26, taken at 0° C, show a time-lag constant of 11 seconds for the electric hygrometer compared to 195 seconds for the hair hygrometer. Considering the zero-degree data and a balloon rate of ascent of 300 meters per minute, the indicated humidity would lag behind the ambient humidity by only 55 meters with the electric hygrometer compared with 975 meters for the hair hygrometer. Below 0° C the hair hygrometer becomes increasingly sluggish, until its time-lag constant becomes infinite at about −40° C [7]. On the other hand, excellent indicated changes in humidity have been obtained in soundings with the electric hygrometer down to −60° C, as will be seen from the following illustrations.

Figures 27 to 29, inclusive, show typical observations with the electric hygrometer which emphasize its high rate of response and indication at low temperatures. These illustrations correspond to the standard adiabatic charts used by meteorologists, in which the abscissas represent temperature and relative humidity and the ordinates

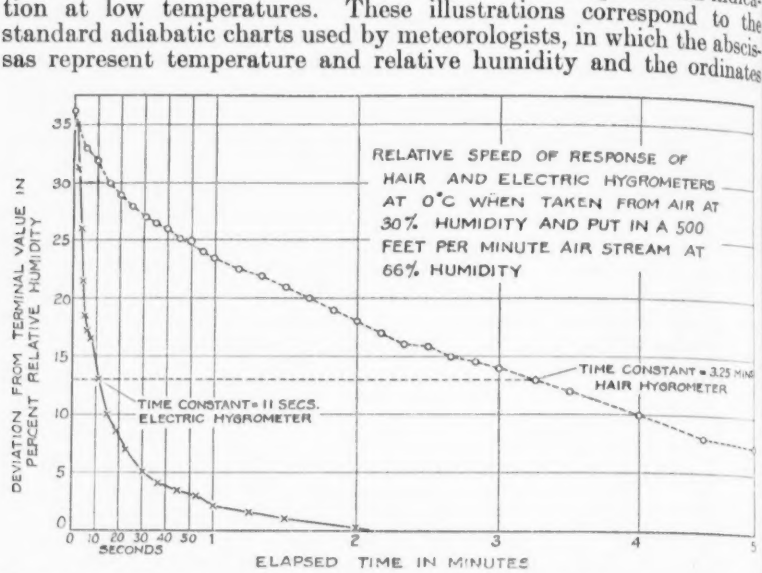
RELATIVE SPEED OF RESPONSE OF HAIR AND ELECTRIC HYGROMETERS AT 0°C WHEN TAKEN FROM AIR AT 30% HUMIDITY AND PUT IN A 500 FEET PER MINUTE AIR STREAM AT 66% HUMIDITY
TIME CONSTANT = 3.25 MINS. HAIR HYGROMETER
TIME CONSTANT = 11 SECS. ELECTRIC HYGROMETER
DEVIATION FROM TERMINAL VALUE IN PERCENT RELATIVE HUMIDITY
SECONDS
ELAPSED TIME IN MINUTES

FIGURE 26.—*Relative speed of response of hair and electric hygrometers at 0° C.*

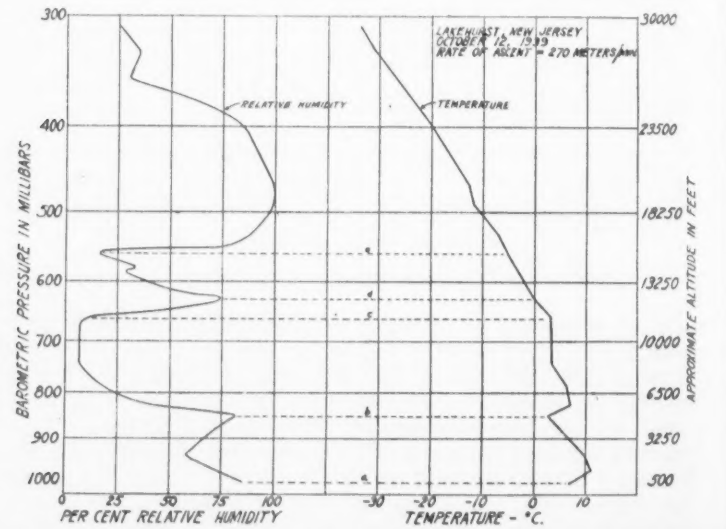

FIGURE 27.—*Results of sounding showing high speed of response of electric hygrometer and indication at low temperatures.*

represent barometric pressure. The temperature observations will serve to indicate the temperatures at which the humidity observations occurred. Discontinuities in the rate of change of temperature with pressure are generally accompanied by corresponding, often sharp, discontinuities in the rate of change of humidity with pressure; it will

be observed that the electric hygrometer indicates these humidity variations quite well. Thus, in figure 27, note that humidity variations are indicated at temperatures below −20° C; in figure 28, at temperatures below −50° C; and in figure 29, at temperatures of about −60° C. Note particularly the excellent correlation between the changes in temperature-lapse rate and in the rate of change of humidity variation at points *a*, *b*, *c*, *d*, and *e* in each illustration.

Figures 30 to 31, inclusive, show comparative soundings with the electric-type and hair-type hygrometers. The greater range of humid-

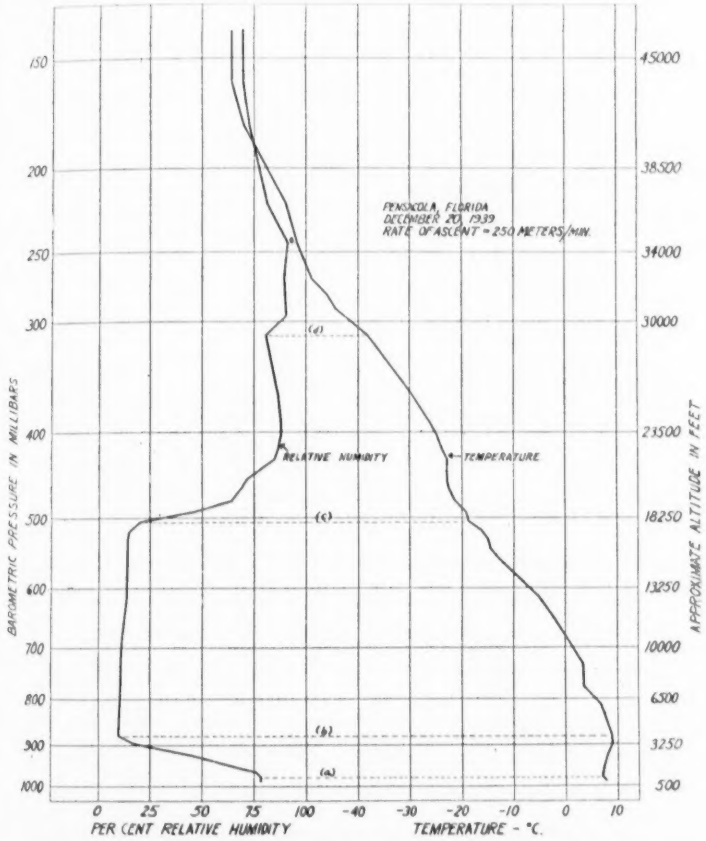

FIGURE 28.—*Results of sounding showing high speed of response of electric hygrometer and indication at low temperatures.*

ity indication with the electric hygrometer, indicating greater speed of response, will be apparent in each illustration. In the case of figure 30, separate balloons were used for carrying the hair-type and electric-hygrometer-type radio sondes. This comparative sounding is of interest in that the temperature remained above 0° C to a height of 7,500 feet; nevertheless, the hair hygrometer shows a marked lag in response. In the soundings corresponding to figure 31, both the hair-type and electric-hygrometer-type instruments were carried on the same balloon.

(c) ACCURACY OF INDICATION

The exact evaluation of the accuracy of the humidity observations with the electric hygrometer does not appear to be practicable in the present state of the art. Laboratory measurements break down for temperatures below about −15° C because of the lack of availability

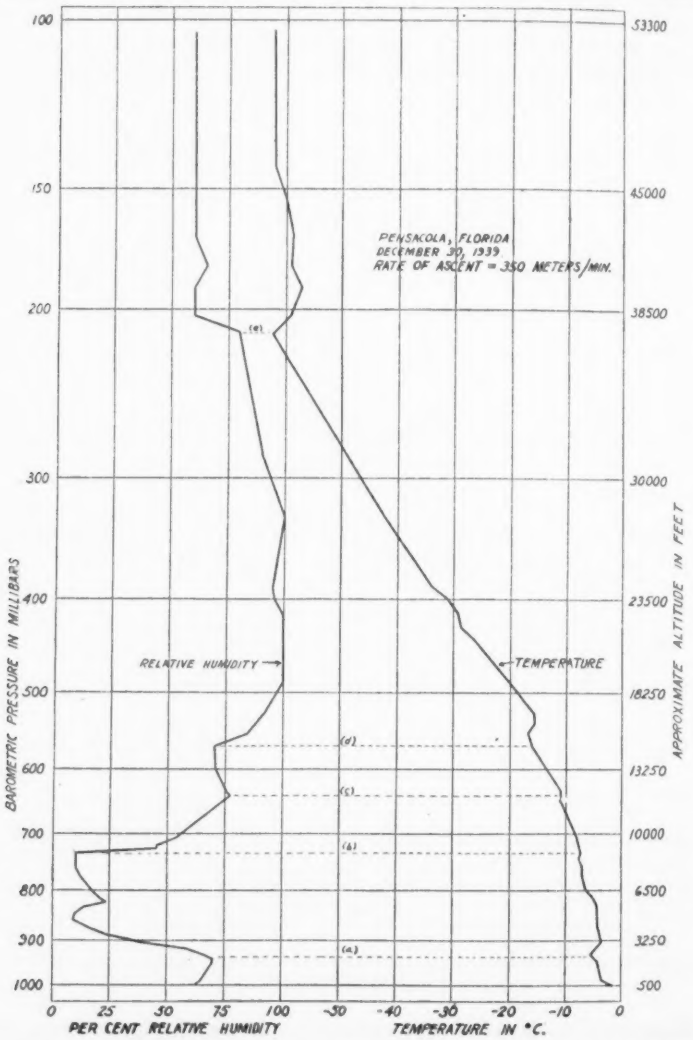

FIGURE 29.—*Results of sounding showing high speed of response of electric hygrometer and indication at low temperatures.*

of a standard comparison instrument. The determination of performance under actual flight conditions is even more difficult because of the low speed of response of the only practicable comparison instrument, namely, the hair hygrometer.

An approximate idea of performance may be had by reference to figure 32. The graphs for this illustration were prepared from data taken at the Naval Air Station, Anacostia, D. C., in the routine surface checks just prior to the soundings. Graph 1 summarizes data for approximately 350 instruments used during April 1, 1939, to March 31, 1940. Graph 2 summarizes the data for the last month of this period. The abscissas represent deviations between the surface humidity observations from the radio-sonde and humidity readings taken with a calibrated psychrometer; the ordinates represent the percentages of the total observations falling within the specified

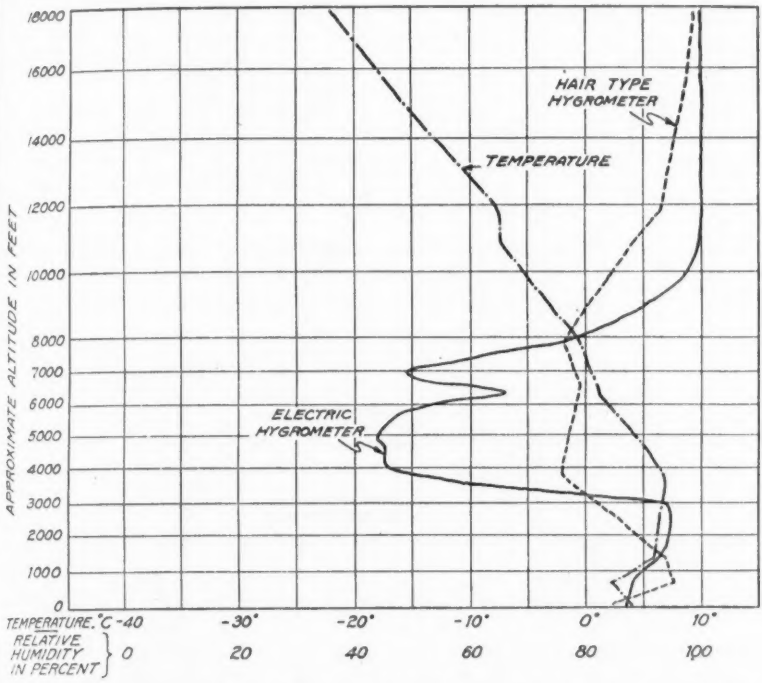

FIGURE 30.—*Comparative soundings with hair-type and electric-hygrometer-type radio sondes.*

Instruments on separate balloons.

deviation. In analyzing the graphs, it should be noted that the pyschrometer readings may be in error up to 3-percent relative humidity.

The improvement shown for the latest month arises from an improvement in the control of aging of the device, recently realized. Further improvement is expected from increased control of the manufacturing processes, now under investigation. On the basis of graph 2, the probable accuracy of the electric hygrometer at surface temperatures is seen to be about 5-percent relative humidity. This accuracy undoubtedly obtains to considerably lower temperatures.

To obtain an idea of the accuracy of indication under flight conditions, some 50 airplane soundings were made almost simultaneously with the regular radio soundings. Because of the better ventilation of the airplane instrument and its lower rate of ascent, 100 meters per minute compared with 175 meters per minute for the average radio sounding, the hair hygrometer in the airplane instrument could be expected to serve as a better comparison instrument. At the same time, the radio-sonde ascent was increased to about 250 meters per minute. Even under these conditions, only those soundings which

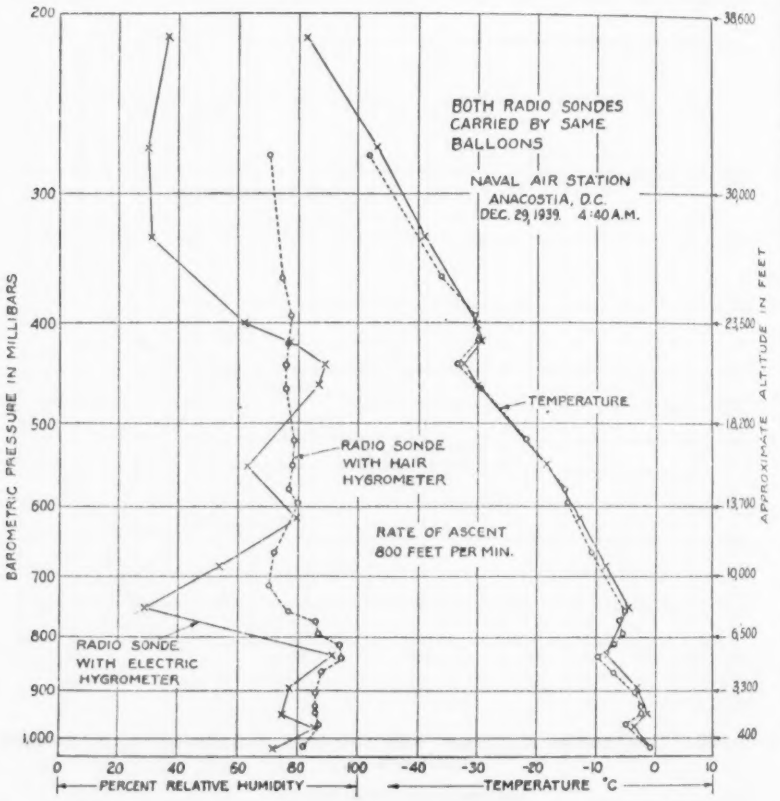

FIGURE 31.—*Comparative soundings with hair-type and electric-hygrometer-type radio sondes.*

Instruments on same balloons.

corresponded to relatively slow changes of relative humidity with height afforded useful comparison data. The data from seven such soundings are plotted in figure 33. The abscissas represent relative humidity and the ordinates barometric pressure. The solid curves correspond to the observations from the electric hygrometer and the dotted curves to the observations from the hair hygrometer. Note that whenever the humidity varies slowly enough so that the lag in the hair hygrometer is not important, the two sets of observations are in relatively good agreement.

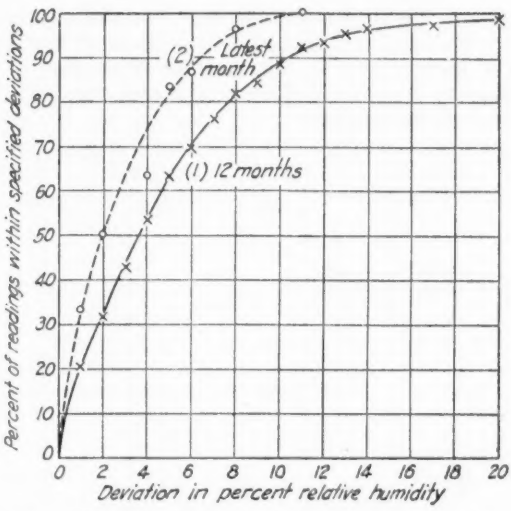

FIGURE 32.—*Analysis of ground checks on electric hygrometer at Naval Air Station, Anacostia, D. C.*

(1) April 1, 1939 to March 31, 1940; (2) March 1 to 31, 1940.

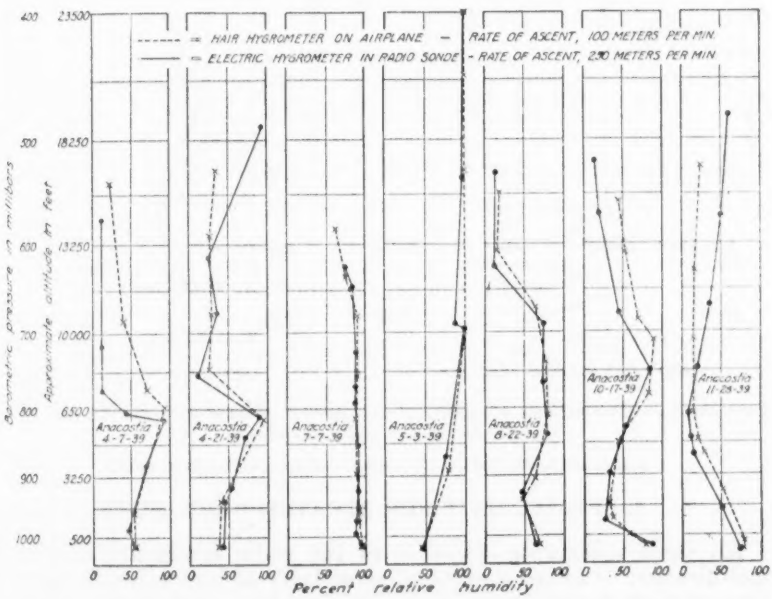
HAIR HYGROMETER ON AIRPLANE — RATE OF ASCENT, 100 METERS PER MIN.
ELECTRIC HYGROMETER IN RADIO SONDE - RATE OF ASCENT, 250 METERS PER MIN.
Barometric pressure in millibars
Approximate altitude in Feet
Anacostia 4-7-39
Anacostia 4-21-39
Anacostia 7-7-39
Anacostia 5-3-39
Anacostia 8-22-39
Anacostia 10-17-39
Anacostia 11-28-39
Percent relative humidity

FIGURE 33.—*Comparative soundings with electric hygrometer in radio sonde and hair hygrometer in airplane instrument.*

Figure 34 shows the humidity data from two radio soundings in which observations were obtained during the descent of the instruments as well as during their ascents. In view of the different geographical locations of the instruments during ascent and descent, the agreement of the observations is excellent.

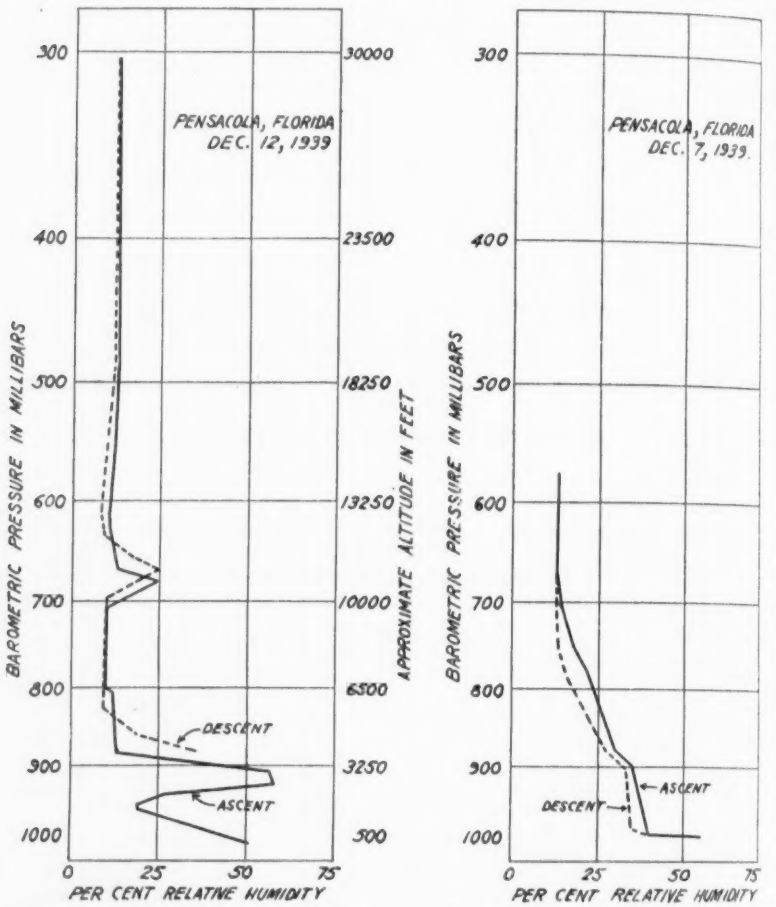

FIGURE 34.—*Comparison of electrical hygrometer observations during ascent and descent in two radio soundings.*

Rate of ascent, 250 meters per minute; rate of descent, 400 meters per minute.

5. SPECIAL UNIT FOR STRATOSPHERE WORK

All three measuring elements of the radio sonde are capable of modification to afford maximum sensitivity of indication in any portion of their respective ranges. This renders possible the design of an instrument specially adapted to stratosphere investigations.

Thus, for the pressure element, the arrangment devised by Brombacher, Goerke, and Cordero [6] may be used, giving measurements

at approximately 2-millibar intervals below about 150 millibars. For the temperature element, a tube having a resistance of 5,000 ohms at +30° C may be used, giving a sensitivity of indication ranging from 2 cycles per degree at −50° C to 1 cycle per degree at −80° C. (See fig. 19.) For the humidity tube, a three-element unit employing sensitive coatings of 3, 6, and 9 percent lithium-chloride solutions, respectively, would give a sensitivity of humidity indications at −50° C equivalent to that now obtained at 0° C, namely, about 1.5 cycles per percent relative humidity.

In conclusion, acknowledgment is made to R. Chappel, L. E. Wood, and K. E. Whitney, of Julien P. Friez & Sons, Inc., for contributions to the practical design of the radio sonde and ground-station equipment, and to C. Brunetti, of Lehigh University, for determining the performance of the radio-sonde transmitter.

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[3] F. W. Dunmore, *An improved electric hygrometer*, J. Research NBS **23** (1939) RP1265.

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WASHINGTON, June 5, 1940.

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RESEARCH PAPER RP1330

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INTEGRATING CIRCUIT FOR VAPOR-TYPE GEIGER-MÜLLER COUNTERS

By Leon F. Curtiss

ABSTRACT

A circuit is described for integrating the pulses from tube counters filled with alcohol vapor and argon and for measuring the output on a rugged milliammeter. These counter tubes require no external quenching device, therefore a simple resistance-capacity coupled amplifier is arranged to amplify and level the pulses. They are then rectified and fed into a condenser with resistance leak. A vacuum-tube voltmeter stage is incorporated in the circuit to measure the voltage of this condenser. This voltage is proportional to the counting rate under the conditions obtained in this circuit.

Two types of portable apparatus, operated from the 110 volt a-c supply, are described which use the circuit outlined above. One is a sensitive counter unit suitable for measuring low gamma-ray intensities, down to the equivalent of 0.1 microgram of radium. The output meter is a milliammeter with a full scale deflection of 1.5 milliamperes. A multirange switch permits operation at several sensitivities. On the most sensitive range the sensitivity is 0.03 milliampere per microgram of radium at 1 meter. The scale of the meter is linear with the counting rate so that comparisons between radioactive sources can be made when desired without reference to the calibration surve. A carefully prepared calibration curve can be used to determine gamma-ray intensities in this region of intensity to within a few percent. The calibration remains comparatively steady over periods of months.

The other apparatus based upon the same circuit is a dosage meter for gamma-rays which indicates on a milliammeter the gamma-ray dosage in terms of roentgens per day and in addition gives a visual and audible alarm when this dosage reaches the tolerance level of 0.1 roentgen per day. At the present time a general exposure of this amount is regarded as safe. This equipment is designed to give warning of excessive general exposures wherever large sources of gamma radiation are present, such as in the use of radium, high-voltage tubes, and cyclotrons.

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I. INTRODUCTION

The properties of alcohol vapor-argon counters [1] are such that considerable simplification of counter control circuits for use with them can be effected. The most important characteristic in this connection is their self-quenching property, which obviates the necessity of any external quenching device, such as a Neher-Harper stage. This self-quenching is operative with comparatively low resistances in the counter circuit, so that the counters are capable of

[1] A. Trost, Z. Physik **105**, 399 (1937).

very rapid counting. It is therefore possible to arrange a simple circuit to amplify and integrate the output from these counters even at the highest counting speeds of which they are capable. A resistance-capacity coupled vacuum-tube circuit has been developed in which the pulses are amplified and leveled and then rectified and used to charge a condenser provided with a resistance leak. A vacuum-tube voltmeter stage with linear scale is used to measure the voltage of this condenser, which is proportional to the counting rate. In developing this circuit, care has been taken to secure a linear scale on an output meter which is rugged and suitable for portable use. Attention has also been given to details of the circuit so that the cumbersome parts could be avoided with no sacrifice of reliability.

This paper describes two forms of portable apparatus which are based essentially upon the same circuit but are intended for quite different uses. One is a sensitive gamma-ray counter which is suitable for measuring intensities down to the equivalent of 0.1 microgram of radium. The output meter of this model is a milliammeter with a full scale deflection of 1.5 milliamperes and has a sensitivity on the highest range of approximately 0.03 milliampere per microgram of radium at 1 meter.

The other device is a relatively insensitive counter unit for indicating gamma-ray dosages near the tolerance level for human exposure. This equipment is provided with a milliammeter calibrated in terms of roentgens per day. It also gives an audible and visual alarm when the general intensity reaches the tolerance level of 0.1 roentgen per day.

II. TUBE COUNTERS FILLED WITH ALCOHOL VAPOR AND ARGON

Numerous suggestions have been offered for the preparation of counter tubes containing alcohol vapor. Particular attention has been given to the treatment of the metal tube in order to produce a satisfactory counter. The type of surface ordinarily formed by oxidation from prolonged exposure to air does not always give satisfactory results in these counters. Some investigators state that copper is quite unsuited for this purpose, unless given some special treatment as by strong oxidation or lacquering. Brass has been reported to be satisfactory after cleaning and oxidizing by exposure to air for several days. The experience of the writer indicates that good results are obtained only when the metal surface of the tube of the counter has been treated in some way. Trials of various methods of oxidation have not yielded uniform results with the same metal. Different metals appear to require various degrees of oxidation.

As a result of experiences of this kind, several types of lacquer have been tried. Coatings of varying thicknesses have been tested, applied in different ways. Best results have been obtained to date by dipping the tube in a dilute solution of commercial Bakelite lacquer and allowing it to dry in the air at room temperature. A dilution to about 10 percent of the original strength in amyl acetate has been found suitable. A coating which is too thick or which has been baked at temperatures above 50° C usually ruins the tube for satisfactory performance in a counter. The fact that the lacquer must be in a soft state suggests that the solvent, amyl acetate, may be responsible

in part, at least, for the properties of the counter tube. Experiments are in progress to determine whether this is the case.

The proportions of alcohol vapor and argon used in filling these tube counters are not critical. It is apparently necessary to have a pressure of approximately 1 cm of Hg of alcohol vapor, regardless of the total pressure in the tube, to secure proper quenching. Counters have been made which operate satisfactorily with around 1,000 volts applied to the tube with total pressures varying from 2 to 8 cm of Hg. Counters of the same size prepared at the same time, as outlined above, usually have the same characteristics, operating within a few volts of the same voltage. Counters have been made as large as 10 cm and as small as 1 cm in diameter. They have shown sensitivities approximately proportional to the area of the longitudinal cross section. After a short aging period, usually a matter of a few days, during which they are permitted to operate continuously, the sensitivity of a given counter remains essentially constant over a period of months.

A study of the curve showing counting rate versus voltage has been made for a number of these counters. To date it has not been found possible to produce counters of this type with any portion of this curve parallel to the voltage axis. However, a "plateau" does exist in which the slope of the straight portion is very slight. For our best counters this is usually of the order of 0.15 percent of the average counting rate per volt applied to the tube. Therefore, a change of a few volts produces no appreciable error. Fortunately, it is possible to stabilize the voltage applied to the counter by means of neon lamps, so that fluctuations are reduced to 2 or 3 volts. The voltage thus obtained is practically independent of the supply voltage over any range usually encountered. A typical curve showing the voltage characteristics of these counters is shown in figure 1. The slope of the straight portion is 0.16 percent per volt over a range of about 100 volts. The data for this curve were taken with a carefully tested scaling circuit which recorded the total number of individual counts for each point. Similar data for different values of the capacity of the condenser used to couple the counter to the amplifier have been taken. Values between 0.00001 microfarad and 0.00005 microfarad have little effect upon the shape of this curve.

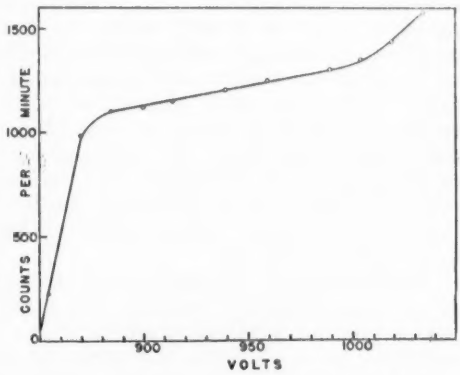

FIGURE 1.—*Characteristic curve voltage versus counting rate, for alcohol vapor-argon tube counter.*

Using the method of lacquering described above, the kind of metal used for the tube of counters filled with alcohol vapor and argon does not seem to be important. Counters have been made with brass, copper, and aluminum tubes and with copper-gauze cylinders as the tubular electrode. These have all shown similar characteristics.

III. THE CONTROL CIRCUIT

The writer has previously described [2] a circuit for integrating and measuring the rate of pulses from counters filled with argon and hydrogen. For this type of counter a Neher-Harper or similar stage is required in the control circuit for high rates of counting, since the argon-hydrogen counters are not self-quenching. The successful use of the Neher-Harper stage requires a bias voltage which must be carefully adjusted and maintained at a constant value. The experience of the writer has been that this adjustment is difficult to make. If the correct adjustment is not made either spurious pulses may easily be introduced, which do not originate in the tube counter, or the full number of pulses may not be measured. Either condition is unsatisfactory. The use of a battery to provide this bias voltage is undesirable in a circuit which otherwise is operated entirely from the a-c supply.

Fortunately the Neher-Harper stage is not required with counters filled with alcohol vapor and argon. The self-quenching properties of these counters are so effective that conventional resistance-capacity coupled stages may be used with comparatively low values of the resistances throughout. This results in circuits which are at least as rapid in response as any using the Neher-Harper arrangement. In addition, all biasing voltages can be eliminated, resulting in a circuit which is easy to adjust and maintain in proper adjustment. Several types of circuits have been tried with various modifications. The requirements of a circuit of this kind are that it shall amplify the pulses and bring them to a uniform size and then measure their rate of occurrence. The simplest way to determine the rate in a high-speed circuit of this type is to rectify the levelled pulses, feed them into a condenser provided with a resistance leak, and measure the potential across the condenser.

The levelling of the pulses from a counter for this purpose has been given considerable attention in recent years. Many investigators prefer to use a multivibrator for this purpose. The multivibrator is adjusted to go through one cycle for each pulse applied to it. The resulting pulses are then assumed to be identical. Tests in this laboratory show that a multivibrator stage must be made up of carefully selected components to function properly and that the circuit constants are usually different for each one assembled from apparently identical parts. Furthermore, the pulse from a multivibrator stage is dependent on the plate voltage, so that uniform pulses are only secured when the plate voltage is carefully regulated. These experiences led to a careful comparison between the output from a multivibrator and a simple triode stage arranged so that each pulse from the counter carried the grid voltage to, or below, the cut-off for the plate current. Each arrangement was found to be equally satisfactory when a stabilized voltage was used for the B supply. However, the multivibrator required frequent adjustment to insure proper conditions for oscillation. Under these circumstances, the simple triode stage is preferable.

The wiring diagram of the complete circuit finally adopted is shown in figure 2. The control circuit proper employs three vacuum tubes,

[2] L. F. Curtiss, J. Research NBS 23, 137, (1939) RP1223.

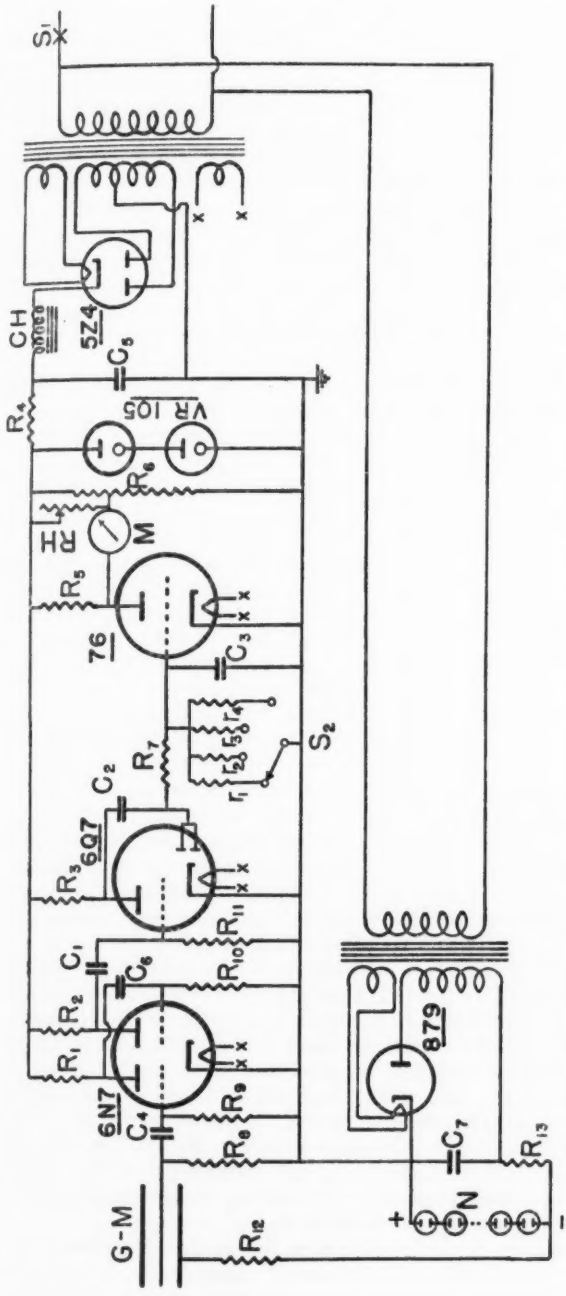

FIGURE 2.—*Wiring diagram for integrating circuit for alcohol-vapor counters with linear output meter.*

C_1, C_4, C_6=0.00005 microfarad
C_2=0.00001 to 0.0005 microfarad
C_3, C_5=8 microfarads
C_7=4 microfarads
RH=0.5 megohm
r_1=1 megohm
r_2=2 megohms
r_3=3 megohms
r_4=5 megohms
R_1, R_2=0.1 megohm
R_3=0.5 megohm
R_4=3,000 ohms
R_5=5,000 ohms
R_6=25,000 ohms
R_7=10 to 15 megohms
R_8, R_9, R_{10}=1 megohm
R_{11}=2 megohms
R_{12}=40 megohms
R_{13}=3 megohms

253356—40——6

one 6N7, one 6Q7, and one 76. The latter tube is used in the vacuum-tube voltmeter stage to measure the voltage of the integrated pulses. The triode section of the 6Q7 is used to level the amplified pulses and the diode section to rectify them in order to charge the condenser, C_1. Since a -4 volt pulse on the grid of the triode section of the 6Q7 is sufficient to bring the plate current to zero at 200 volts on the plate, a moderate amplification of the counter pulses would be sufficient to insure that all pulses were levelled to the same value. However, a negative pulse is required so that two triode stages are introduced between the counter tube, *G–M*, and the 6Q7. This is done by use of the two triode sections of a 6N7 vacuum tube. Under these conditions, it is quite safe to assume that all pulses originating in the counter throw the grid of the 6Q7 to cutoff. Numerous tests with an oscillograph and by comparison with scaling circuits show that this assumption is justified.

It is desirable that the meter, *M*, in the vacuum tube voltmeter stage, shall show a response which is linear with the grid voltage. This is secured by introducing a bucking circuit comprising the resistor, R_5, and the rheostat, *RH*, in conjunction with the voltage divider as shown. The part of the plate current of the 76 tube which passes through the meter, *M*, is controlled by the rheostat, *RH*, and permits an adjustment of the meter to a zero reading for any particular background intensity in the presence of which measurements are to be made. The arrangement shown permits a very accurate adjustment of the zero of the meter, since the meter current changes slowly and smoothly with changes of the value of *RH*. A simple rectifier and filter supply the plate voltages for the circuit. This voltage is held at a steady value regardless of line-voltage fluctuations by the VR-105 regulator tubes. A half-wave rectifier using an 879 tube supplies the voltage for the counter tube. This voltage is also stabilized by a bank of small neon lamps, *N*. These lamps give good regulation, particularly after they have been aged by burning steadily for several hours.

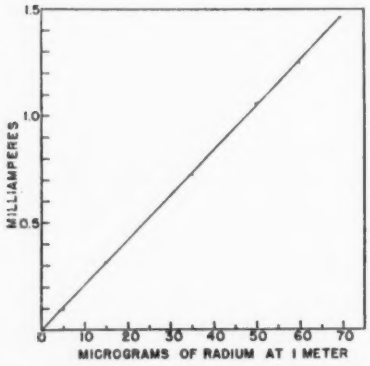

FIGURE 3.—*Typical calibration curve at high sensitivity.*

The advantages of this circuit are that it is simple, low resistances are used throughout, it requires no preliminary adjustment of constants, no bias voltages are used, and its indications are directly proportional to the counting rate. The small number of parts permits it to be mounted in a single aluminum case. By putting the RC circuit of the voltmeter in the grid, a small condenser can be used and a number of ranges selected readily by cutting in the resistors, r_1, r_2, r_3, r_4, by means of the rotary tap switch S_2.

A typical calibration curve is shown in figure 3. The readings for the points shown were obtained by placing microgram radium standards at a distance of 1 meter and noting the final steady deflection of the milliammeter. Approximately 5 minutes is required for the RC

circuit to come to an equilibrium value. The sensitivity here shown is 0.021 milliampere per microgram of radium and was obtained with 3 megohms and 8 microfarads in the RC circuit of the voltmeter stage. The sensitivity is increased to 0.033 milliampere per microgram of radium at 1 meter when 4 megohms are used in this circuit. At this sensitivity 1 microgram of radium at 25 cm gives a deflection of about 0.5 milliampere, or about one-third of a full-scale deflection on the meter. Our experience indicates that this circuit retains its calibration over periods of months. Figure 4 shows a complete set of calibration curves for all four ranges of one of the instruments. The values of the resistances, r_1, r_2, r_3, and r_4, are 1, 2, 3, and 5 megohms. For $r_1=1$ megohm, 300 micrograms of radium are required for a full-scale reading of 1.5 milliamperes; and for $r_4=5$ megohms, 35 micrograms give the same reading. This is about as large a range as can be covered with a given size of counter tube.

The sensitivity of this equipment can also be controlled by changing the size of the counter or the value of the coupling condenser, C_2. For large steps in sensitivity, a counter of different size must be used. This circuit will work well with counters as large as 10 by 40 cm and as small as 1 by 1 cm. Sizes outside this range have not been tried.

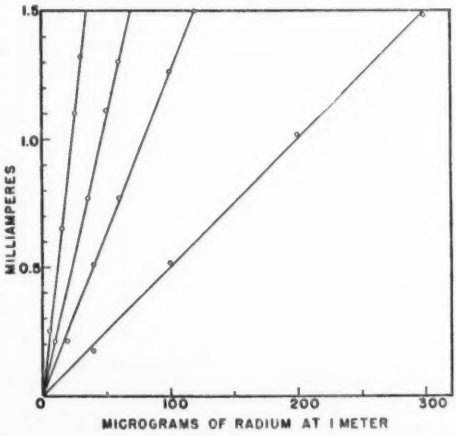

FIGURE 4.—*Group of calibration curves for a multirange instrument.*

The linear characteristic of the output meter makes it convenient to measure gamma-ray intensities by direct comparison with microgram standards of radium. For most accurate measurements, a direct comparison, selecting a standard somewhere near the value of the unknown, permits measurements to be made independently of the original calibration. Gamma-ray standards for this purpose consisting of ampoules containing 5 ml of solution and having radium contents of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 50.0, and 100.0 micrograms are now available at the National Bureau of Standards.

The compactness of the circuit permits it to be built into a single cast-aluminum case 7 by 6 by 18 in. The case is provided with short standards bored to hold the tube counter. Thorough ventilation is required as a result of the considerable heat developed by the rectifier tubes. This is secured by numerous perforations in the top and bottom of the case. The milliammeter, M, is mounted in the top of the case for ease of observation. The knobs of the range switch, S_2, and of the bucking circuit rheostat, RH, are brought out at the side. The total weight, most of which is in the transformers, is 24 lb. A view of the interior of this case, with parts in place, is shown in figure 5, and an exterior view in figure 6.

IV. RADIO EXPOSURE METER

The use of alcohol vapor-argon counters also permits considerable improvement in the radium exposure meter described by the author.[3] The same basic circuit as shown in figure 2 is used for this meter. The only changes are in the vacuum-tube voltmeter stage. The range switch, S_2, and the bucking circuit, including R_7 and RH, are eliminated. The modifications added are shown in figure 7. A relay, Z, is connected in series with the milliammeter, M. A buzzer, B, and lamp, L, are connected in the contact circuit of the relay which closes this circuit through a low voltage winding on the power transformer. The tension of the relay spring is adjusted to close the contact at the desired value of the current in the meter, M.

For this instrument a small counter, 1 by 1 cm, is required because of the relatively high intensity of gamma radiation to be measured. It is also important to use a counter with a length approximately equal to the diameter so that it may have the same sensitivity in all directions. These smaller counters have a voltage characteristic similar to that of the larger counters and will operate over about the same range of voltages, 700 to 1,000 volts.

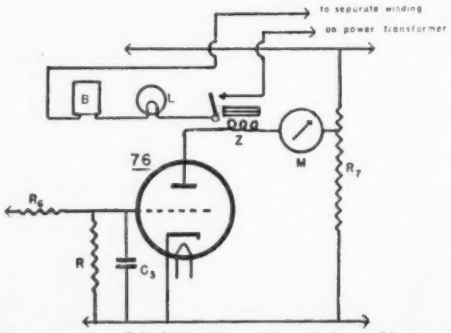

FIGURE 7.—*Modification of wiring diagram shown in figure 2, as used in radium exposure meter.*

As a result of the elimination of the bucking circuit, the meter scale is not linear in this instrument and the meter reads downward for increasing intensities. The scale is almost identical with that described for the argon-hydrogen counters.[4] The relay is adjusted to close when the intensity reaches the value of 0.1 roentgen[5] per day, providing a visual and audible warning of excessive general exposure.

Although this meter was originally designed for use in hospitals and laboratories where large quantities of radium are handled, it is obvious that it can be used equally well in connection with high-voltage installations or cyclotrons where artificial gamma radiation is generated. The most satisfactory method of use is undoubtedly as a monitor, placing the instrument at a position habitually occupied by operators. It can also be used to survey a laboratory under given conditions of operation to determine certain zones of safety under these conditions. Such a survey would, of course, need to be repeated when changes were made in the operation of the source. For complete protection in a large installation, several units properly located would be required. It would be desirable to have them switched on automatically with the source. Warning would then be given of any unsafe conditions which arise from an increase in the gamma-ray intensity as a result of unforeseen changes in the apparatus generating the artificial radio

[3] L. F. Curtiss, J. Research NBS **23**, 479 (1939) RP1246.
[4] L. F. Curtiss, J. Research NBS **23**, 479 (1939) RP1246.
[5] At the present time a general exposure of 0.1 roentgens per day of 8 hours is regarded as safe. See Handbook H23, NBS, on Radium Protection.

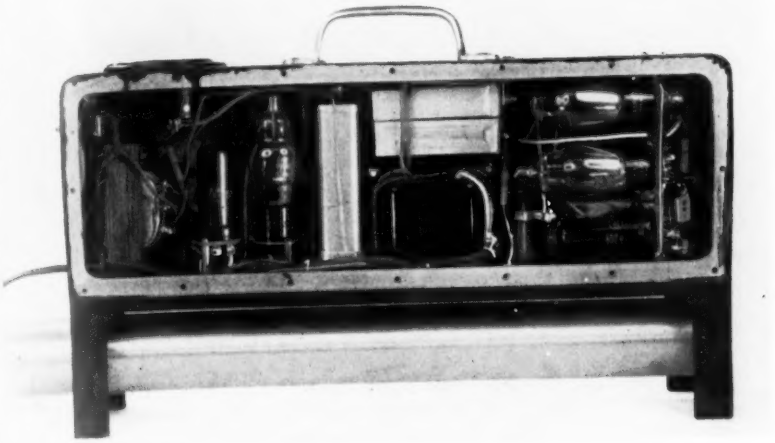

FIGURE 5.—*Interior view of assembled gamma-ray counting-rate meter.*

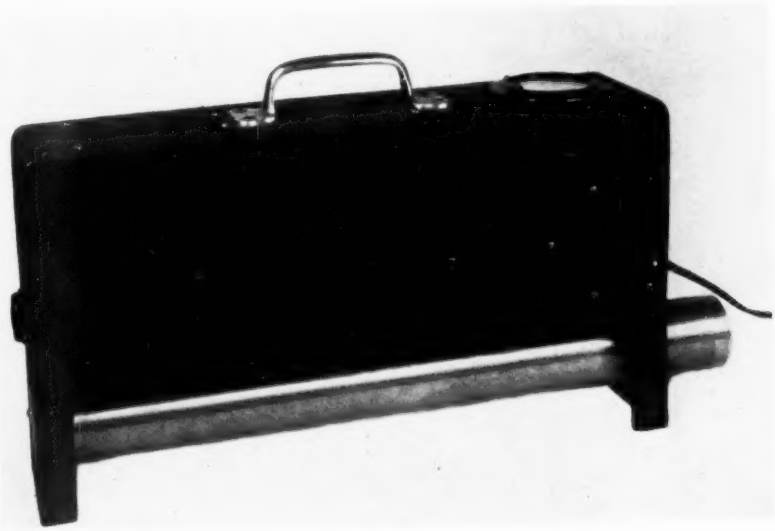

FIGURE 6.—*Exterior view of gamma-ray counter.*

activity. When equipped with a boron trifluoride tube counter, this device is also useful in warning of dangerous intensities of neutrons. The low efficiency of these counters makes this somewhat difficult. Experiments are in progress to determine the proper arrangements for a warning device of this type.

The writer acknowledges the aid of L. L. Stockmann and B. W. Brown in assembling and testing these units. He is also indebted to A. V. Astin for advice regarding various details of the amplifying and integrating circuit.

WASHINGTON, July 2, 1940.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1331

Part of Journal of Research of the National Bureau of Standards, Volume 25, September 1940

DECOMPOSITION OF ROCKS AND CERAMIC MATERIALS WITH A SMALL AMOUNT OF SODIUM CARBONATE

By James I. Hoffman

ABSTRACT

A method for the decomposition of rocks and ceramic materials is presented in which only 2 parts of sodium carbonate are used for 1 part of sample. The fusion is made in a 75-ml platinum dish instead of a crucible. If silica is to be determined, the same dish is used for the fusion, the disintegration of the melt with hydrochloric acid, the evaporation to dryness, and the ignition of the silica.

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I. INTRODUCTION

For the decomposition of rocks and ceramic materials, fusion of 1 part of sample with 4 to 10 parts of sodium carbonate is usually recommended. The large amount of sodium salt thus introduced is often undesirable in the determinations which follow. The desirability of using smaller amounts of flux was recognized by Finn and Klekotka,[1] who showed that certain ceramic materials, for example, clay, feldspar, and high-alumina refractories, can be successfully broken up by sintering at 825° to 950° C with a portion of sodium carbonate approximately equal to the weight of the sample. Decomposition by sintering is satisfactory provided that the most suitable sintering temperature and quantity of sodium carbonate have been determined. In the method which follows, the quantity of flux and temperature of fusion are the same for all the materials.

The experiments on fusions with less than the customary amounts of sodium carbonate were started primarily to develop a method for determining the silica content of glass and of certain ceramic materials by a single dehydration. After many trials, it was found that satisfactory results could not be obtained by single dehydrations,[2] but the

[1] A. N. Finn and J. F. Klekotka, BS J. Research 4, 809 (1930) RP180.

[2] The method which came closest to giving satisfactory results for silica in glass in one dehydration is one developed by P. A. Webster and A. K. Lyle of the Hartford-Empire Co., Hartford, Conn. (private communication). Their method is similar to the one described herein, except that nitric acid is used to decompose the fused mass and perchloric acid is used for the dehydration. Seldom does more than 0.1 percent of the silica remain in solution with their method, but it was found that no method, when applied to miscellaneous materials, is entirely dependable unless two dehydrations are made. [While this article was in press Webster and Lyle's method appeared in J. Am. Ceram. Soc. 23, 235 (1940).]

decomposition of the various materials was so successful that it seemed worth while to extend the study to a wider range of ceramic materials, and also to rocks and minerals.

Disintegration of the melt obtained with the method described in this paper leaves practically all the silica as a residue, whereas a clear or nearly clear solution is obtained by similarly treating a melt obtained by fusing with a large quantity of sodium carbonate. The results of this study indicate that the amount of nonvolatile matter retained by the insoluble mass that results from disintegration of the former melt is about equal to that which is adsorbed and retained by the gelatinous silicic acid which separates during the evaporation of the clear solution obtained from the latter melt. The fact that inspection does not immediately show whether decomposition has been complete when only a small amount of sodium carbonate has been used may account for the almost universal use of unnecessarily large quantities of flux. Furthermore, the earlier analysts did not have furnaces in which uniform temperatures of about 1,200° C could be maintained.

II. METHOD FOR THE DETERMINATION OF SILICA

Transfer 0.5000 g of the finely ground sample (60 mesh or finer) and 0.50 g of sodium carbonate to a 75-ml platinum dish,[3] and intimately mix the contents by means of the flattened end of a glass rod. If the sample contains ferrous iron or much lead, add 0.05 g of potassium nitrate to prevent alloying of the platinum dish. Brush the mixture into the center of the dish, flatten the charge so that it covers a space about 3 cm in diameter, and then cover it as evenly as possible with an additional 0.50 g of sodium carbonate. Heat gradually at first (preferably in a muffle furnace) and finally at 1,200° C for 15 minutes.[4] Remove the dish from the source of heat, and cover it to prevent loss of small pieces of the solidified melt that might be ejected during cooling.

Add 20 ml of diluted hydrochloric acid (1+1)[5] to the cooled melt, cover the dish, and digest on the steambath until disintegration is complete. The action of the acid can be hastened by occasionally crushing the layer of insoluble silica that tends to cover the unattacked portion of the fused mass. As soon as disintegration is complete, crush all flakes of solid matter with the flattened end of a glass rod. Evaporate to dryness on the steambath, cool, drench the dry residue with 5 ml of hydrochloric acid, and then add 15 ml of warm water. Digest on the steambath for a few minutes, and filter through a 9-cm filter of loose texture (No. 40 Whatman or equivalent). Thoroughly wash the dish and filter paper with hot hydrochloric acid (2+98),

[3] Dishes such as are used in determinations of alkalies are satisfactory. Part of this work was done with 50-ml dishes made of platinum alloyed with about 2 percent of iridium. The remainder was done with special long-lipped 75-ml dishes of platinum alloyed with 3.5 percent of rhodium. The latter dishes, weighing about 40 g, were preferable because they are not readily bent out of shape and because the solutions can be poured onto the filter more easily.

[4] A temperature of 1,200° C is specified, but this may be regarded as a maximum because nothing is gained by heating to a higher temperature than that required to give a clear melt. Even at 1,200° C, some high-alumina refractories will yield only a sintered mass, not a clear melt. The decomposition, however, is complete.

[5] This denotes 1 volume of concentrated hydrochloric acid, sp gr 1.18, diluted with 1 volume of water. Diluted hydrochloric acid (2+98) denotes 2 volumes of hydrochloric acid, sp gr 1.18, diluted with 98 volumes of water. If no dilution is specified, the concentrated reagent is meant.

but make no attempt to transfer all the silica from the dish to the paper. Place the filter containing the silica in the platinum dish in which the fusion and dehydration were made, and evaporate the filtrate to dryness on the steambath in another dish, preferably of platinum. Cool, drench the dry residue from the filtrate with hydrochloric acid, dilute, filter, and wash as before. Transfer all the silica obtained in the second dehydration to the paper, and then place this paper also in the platinum dish in which the fusion was made.

Ignite the contents of the dish slowly at first and finally for ½ to 1 hour at 1,200° C. Cool in a desiccator and weigh. Treat the ignited residue with a few drops of diluted sulfuric acid (1+1) and about 10 ml of hydrofluoric acid. Evaporate the volatile constituents on the steambath, drive off the sulfuric acid by heating over a free flame, and finally ignite the residue for 1 to 2 minutes at 1,200° C. The difference between the first and second weights, with a proper correction for a blank for the reagents, represents the silica in the sample.

TABLE 1.—*Typical results obtained for silica and "R_2O_3" in various materials*

No.	Material (0.5-g samples)	SiO_2		Nonvolatile residue by method employing 1 g of Na_2CO_3	"R_2O_3" [a]	
		By method employing 4 to 10 g of Na_2CO_3 in fusion	By method employing 1 g of Na_2CO_3 in fusion		By method employing 4 to 10 g of Na_2CO_3	By method employing 1 g of Na_2CO_3
		Percent	*Percent*	*g*	*Percent*	*Percent*
1	NBS Standard Feldspar 70	66.66	66.62	0.0005	18.07	18.08
2	NBS Standard Feldspar 70	66.66	66.70	.0010		
3	NBS Burnt Refractory 76	54.68	54.76	.0059		
4	NBS Burnt Refractory 77	32.38	32.34	.0033		
5	NBS Burnt Refractory 78	20.69	20.70	.0098	74.92	74.84
6	NBS Standard Glass 128	69.51	69.46	.0004	1.96	2.00
7	NBS Standard Glass 128	69.51	69.56	.0005		
8	NBS Standard Flint Clay 97	42.87	42.80			
9	Basalt (E. page 38) [b]	57.87	57.98	.0027		
10	Keratophyre (G. page 31)	72.73	72.62	.0015	16.52	16.56
11	Quartz monzonite (C–2 page 12 and 13)	69.01	68.98	.0023	18.88	18.90
12	Reddish andesite (F. page 37)	55.18	55.12	.0029		
13	Cyrtolite (Bedford, N. Y.)	31.27	31.31	.0207	55.54	55.58
14	Cyrtolite (Bedford, N. Y.)	31.27	[c] 31.34	[c] .0069	55.54	55.68
15	Chlorite (Vt.)	25.22	25.24	.0016		
16	Granite (Alaska)	73.12	73.20	.0015		
17	Hornblende	62.80	62.88	.0016		
18	Soil (Texas) [d]	65.66	65.74	.0008	8.15	8.19
19	Rhyolite	74.72	74.88	.0022		
20	Miscellaneous samples of limestones, clays, quartz, lead-bearing glass, and bauxite were completely decomposed, but SiO_2 was not determined					
21	Alundum cement and 120-mesh *RR* Alundum were not satisfactorily decomposed					

[a] "R_2O_3" represents the total residue obtained by adding a slight excess of ammonium hydroxide to the filtrate obtained from the determination of silica, filtering, dissolving the precipitate in acid, reprecipitating with ammonium hydroxide, and igniting to constant weight. The residue left after volatilizing the silica was fused, the melt was dissolved, and the solution added to the filtrate from the silica before the precipitation with ammonium hydroxide.

[b] The references following materials 9, 10, 11, and 12 are the designations in U. S. Geological Survey Bulletin 878, from which the values for SiO_2 are taken and where complete analyses are given.

[c] Sulfuric acid dehydration.

[d] Other constituents of the soil from Texas are CaO, 7.11 percent; MgO, 0.77 percent; and SO_3, 8.59 percent.

III. DISCUSSION OF THE PROCEDURE AND RESULTS

Typical results obtained in the determination of silica and "R_2O_3" are shown in table 1. There is no particular advantage in fusing with the small amount of sodium carbonate for determining "R_2O_3" if two precipitations with ammonium hydroxide are made, but these results are included for completeness and to show that the method can be used for this determination.

The use of the same platinum dish for the fusion of the sample, the disintegration of the melt, the evaporation to dryness, and the ignition of the silica approximately halves the time and labor required for a determination of silica and reduces the chances of losses that might occur in the transfer from one vessel to another. In fusing the materials listed in table 1, there was no frothing or spattering, and consequently no occasion for covering the dishes. This is the more surprising because some of the materials, for instance clay and bauxite, contain a considerable percentage of volatile matter.

The nonvolatile residues shown in table 1 are not abnormally large. In the analysis of high-alumina burnt refractories, such residues often weigh more than 5 mg, even if the usual large amount of sodium carbonate has been used in the fusion. Nonvolatile residues do not always indicate incomplete decomposition. They may result from incomplete solution of salts after dehydration of the silica, as is usual with materials high in alumina, or the material (for example, cyrtolite) may contain tantalum and columbium, both of which practically quantitatively accompany silica in any method. With materials such as burnt refractories (high in Al_2O_3) or cyrtolite (high in ZrO_2), it was found advantageous to use sulfuric acid for the dehydrations, because the nonvolatile residues were always smaller.

The results in table 1 indicate also that this method of decomposition is applicable to many minerals and nearly all kinds of rocks and ceramic materials except fused alumina. With such alumina an increase of the temperature to 1,300° C does not effect complete decomposition, and attack on the platinum dishes becomes serious. By mixing 1 part of 90-mesh *RR* Alundum with 1 part of sodium carbonate and 1 part of fused borax, and heating for 15 minutes at 1,200° C, a melt was obtained which left an insoluble residue of only 1.3 mg when the fused mass was treated with a mixture of hydrofluoric and hydrochloric acids. Such a fusion, however, is not satisfactory for the determination of silica because of serious contamination of the silica by boron. Ordinarily, boron can be eliminated by evaporation with methyl alcohol and hydrochloric acid, but when such a small amount of flux is used, disintegration of the melt with hydrochloric acid leaves the silica in rather hard flakes, from which the boron apparently cannot be removed by the usual treatment.

Fusions and ignitions in platinum dishes at 1,200° C always cause a loss of 1 to 2 mg of platinum in a determination, but the dishes are never damaged unless reducing substances, such as ferrous iron, are present. The addition of potassium nitrate prevents damage from this source and is recommended if the material contains much lead [6]

[6] Samples of lead-barium glass containing 17.5 percent of PbO were decomposed by heating to 1,200° C with the recommended amounts of sodium carbonate and potassium nitrate, without any damage to the dishes.

or ferrous iron. The loss of platinum by volatilization does not affect the results for silica unless it occurs after the treatment with hydrofluoric and sulfuric acids. Owing to the relatively large surface of these dishes, as compared with crucibles, a long period of ignition at this point may result in high values for silica. For this reason a short period of ignition of the nonvolatile residue is recommended.

It is often desirable to precipitate iron, aluminum, calcium, and magnesium from solutions containing only small quantities of sodium salts, and it is probable that the method described will find application in other determinations in which large amounts of sodium salts are objectionable.

Acknowledgment is made to R. C. Wells and J. G. Fairchild, of the U. S. Geological Survey, who furnished many of the samples of rocks used in this work.

WASHINGTON, July 18, 1940.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1332

Part of Journal of Research of the National Bureau of Standards, Volume 25, September 1940

THICKNESS OF A LIQUID FILM ADHERING TO A SURFACE SLOWLY WITHDRAWN FROM THE LIQUID

By Francis C. Morey

ABSTRACT

When a solid body is immersed in a bath of liquid and withdrawn, a film of the liquid adheres to the solid surface and gradually drains back into the bath when the motion ceases. The relationship existing between the average film thickness, the speed of withdrawal, and the kinematic viscosity of the liquid is the subject dealt with in this paper.

According to the generally accepted theory the film thickness varies with the square root of the product of the speed and the kinematic viscosity. It was noticed that corrections based on this relationship and used in the calibration of a gas-measuring standard were not satisfactory. Therefore an experimental apparatus was designed to test the theory. Analysis of the data revealed that within the range of speeds used the theory does not correctly predict the film thickness, and an empirical equation of the form

$$t = k\,(\nu s)^n$$

was employed, in which t is the average film thickness, ν is the kinematic viscosity of the liquid, s is the speed of withdrawal of the surface, k and n are quantities varying slightly with the liquid used. The approximate values of k and n found by experiment are 0.015 and 0.63, respectively.

Nine liquids were tested, including mineral, vegetable, and animal oils, and synthetic organic compounds of oily nature.

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I. INTRODUCTION

When a solid surface such as a sheet of metal is withdrawn from a bath of liquid, a thin film of the liquid is carried up with the solid and adheres to it, gradually draining back into the bath if the motion of the plate ceases. In many experiments with physical apparatus it is desirable to know how the thickness of such a film is related to the properties of the liquid and to the speed of withdrawal. Need of such information has occurred in the field of gas measurements, where gas volumes are determined by the displacement of the cylindrical bell of a gas holder moving in a liquid sealing bath. The Stillman portable cubic-foot standard and the gas-meter prover are examples.

Often the liquid film is of negligible volume, especially when the speed of withdrawal is small and where liquids of low viscosity may be used. Research in the method of testing Stillman standards has indicated the desirability of using oil of low vapor pressure as a sealing medium. Such oils have relatively high viscosity, and hence we are faced with the necessity of making small volume corrections due to the oil which adheres to the drum of the instrument.

In reviewing the literature on the subject, it was found that the problem has been investigated by the Research Staff of the General Electric Co. of London,[1] who found that the thickness follows the equation

$$t=\sqrt{\frac{2v_0\eta}{\rho g}},$$

where

t = the thickness of the film near the surface of the bath,
v_0 = the speed of withdrawal,
η = the absolute viscosity of the liquid,
ρ = the density of the liquid,
g = acceleration due to gravity.

This equation is said to apply to a smooth plate of infinite breadth, but will fit the practical case of a cylinder provided the radius of the cylinder is very much greater than the film thickness. The nature of the surface withdrawn is thought to have no importance if the surface irregularities are small relative to film thickness (that is, the surface should be smooth and polished).

Mathematical investigations of the profile of a draining film have been conducted by H. Jefferys,[2] which indicate that the profile of the film is parabolic, at least near the top of the wetted portion. This conclusion has been substantiated by the experimental work of Satterly and associates.[3 4 5 6 7 8]

Additional refinements in the theory have been suggested by Green [9] to account for slight discrepancies observed near the upper boundary of the film.

Use of the equation stated above to compute the correction to apply in calibrating a cubic-foot standard was not entirely satisfactory, and it was therefore decided to attempt to check the equation using the oil selected as a sealing medium. This is a water-white petroleum oil having an absolute viscosity of about 0.24 poise at 25° C and a density of 0.841 g/ml. It was later decided to extend the investigation to include three other petroleum oils and representative vegetable and animal oils and synthetic organic substances of oily nature.

[1] Goucher and Ward, Phil. Mag. [6] **44,** 1002 (1922).
[2] H. Jefferys, Proc. Cambridge Phil. Soc. **26,** 204 (1930).
[3] Satterly and Mills, Trans. Roy. Soc. Can. **21,** 277 (1927).
[4] Satterly and Turnbull, Trans. Roy. Soc. Can. **23,** 95 (1929).
[5] Satterly and Douglass, Trans. Roy. Soc. Can. **24,** 87 (1930).
[6] Satterly and Collingwood, Trans. Roy. Soc. Can. **25,** 215 (1931).
[7] Satterly and Stucky, Trans. Roy. Soc. Can. **26,** 131 (1932).
[8] Satterly and Givens, Trans. Roy. Soc. Can. **27,** 145 (1933).
[9] G. Green, Phil. Mag. [6] **22,** 730 (1936).

II. EXPERIMENTAL APPARATUS

Figure 1 is a schematic diagram of the apparatus used. Determination of the quantity of oil adhering to the surface was accomplished by weighing. A thin brass cylinder, *T*, approximately 6.5 cm in diameter and 27 cm in length, was constructed from brass shim stock 0.013 cm thick. The joint was carefully soldered, and the cylinder was polished inside and outside. It was suspended beneath the table from one arm of an analytical balance, *W*, by means of a fine wire passing through small holes in the case and table so as to

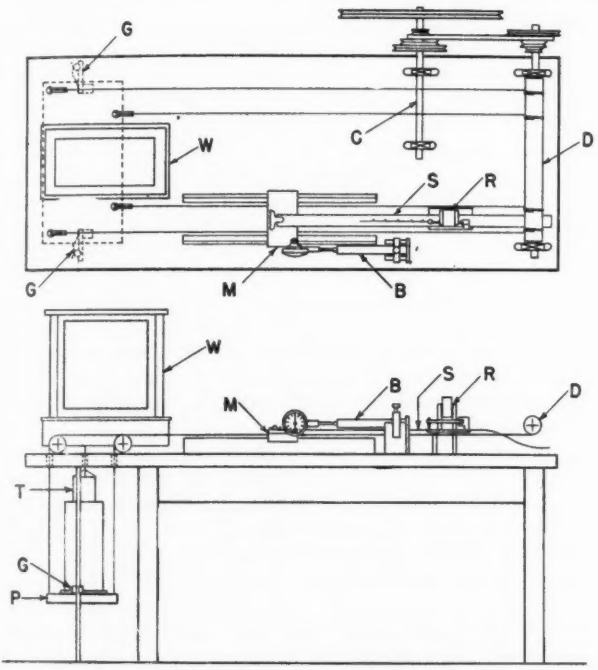

FIGURE 1.—*Schematic diagram of apparatus.*

dip into an oil bath carried on a movable platform, *P*. The clean, dry cylinder was counterbalanced by a tare weight.

The platform, *P*, was supported by four strands of piano wire which passed over pulleys and were attached to the hoisting drum, *D*. The drum was driven by a four-step cone pulley and V-belt speed changer from a countershaft, *C*. The countershaft was belted to the motor drive, which consisted of a ¼-horsepower electric motor operating through a worm-speed reducer to deliver approximately 15 rpm. With such reduction in speed the motor was running practically idle, and changes in frictional resistance or in the load on the platform could not greatly affect the speed or the starting time of the motor.

The platform was guided by two spring friction clamps, *G*, which operated on vertical rods. This eliminated swinging of the platform and damped out most of the vibrations introduced by the motor drive.

In order to control the length of travel of the platform, a carriage, *M*, was mounted on parallel ways and attached by means of a clamping bar to two of the piano wires supporting the platform. To this carriage was bolted a dial indicator in a horizontal position, so as to contact a bar of steel, *B*, of known length. The platform was raised very slowly until contact of the oil with the test cylinder was just established; the carriage, *M*, was then clamped to the wires and the reference reading of the dial indicator noted. A shorter bar was then substituted and the platform raised slowly until the same reading was established on the indicator. The immersion of the cylinder was then equal to the difference in the lengths of the bars. Five bars were provided so as to give immersion lengths of 3, 5, 10, 15, and 25 cm.

The platform was lowered at seven known rates of speed ranging from about 0.1 cm/sec to 1.4 cm/sec. It was felt that within this speed range there would be no significant difference between withdrawing the cylinder from a stationary bath or lowering the bath from a stationary cylinder. The speed of the platform was measured by means of a chronograph strip, *S*, attached to the carriage. A magnetic recording pen, *R*, marked half-second signals on this strip. By using a ruled paper or by measuring the distance between any two marks of the record, it was possible to determine the average speed of the platform throughout the time interval selected. The speed was found to be uniform within about 3 percent, and the time of starting was negligibly short.

For each liquid at least 35 sets of observations were obtained, each set consisting of two trials, the weighings of which were averaged.

The platform, test cylinder, and oil bath were enclosed by a removable shield to eliminate air currents; and the entire apparatus was placed in a room whose temperature was kept uniform within about one degree centigrade by forced air circulation. With the two lightest petroleum oils the air inside the test chamber was kept nearly saturated with the oil vapor, since the oil was found to have a vapor pressure nearly as high as that of water at room temperature. This procedure largely eliminated evaporation of the film from the test cylinder during weighing.

III. DATA AND ANALYSIS

Data on the behavior of nine liquids were obtained. Four of these were petroleum oils, three were synthetic organic compounds, one was a vegetable oil, and two were oils of animal origin. These liquids, with their viscosities and densities, are listed in table 1. Mineral oils 1 and 3 were water-white oils, and number 2 was a blend of these two. Number 4 was a commercial automobile engine oil.

TABLE 1.—*Densities and kinematic viscosities of the liquids tested*

Liquid	20° C		30° C	
	Density	Kinematic viscosity [a]	Density	Kinematic viscosity [a]
	g/ml	*Stokes*	*g/ml*	*Stokes*
Mineral oil 1	0.7862	0.02526	0.7790	0.02049
Mineral oil 2	.8336	.1820	.8268	.235
Mineral oil 3	.8445	.3685	.8377	.2306
Mineral oil 4	.9009	1.008	.8946	.5387
Dibutyl phthalate	1.0464	0.1926	1.0382	.1275
Aroclor (chlorinated diphenyl)	1.3853	.6345	1.3757	.2765
Peanut oil	0.9143	.8949	0.9075	.5896
Sperm oil	.8794	.4062	.8727	.2800
Lard oil	.9140	1.064	.9072	.6749

[a] Accuracy about 0.3 percent relative to the value of 0.01005 poise for the absolute viscosity of water at 20° C.

Preliminary examination of the data revealed that an equation of the type

$$t = k'(\nu s)^n \tag{1}$$

could be used to represent the results, wherein

t = average film thickness, computed from the observed weight and known density of the oil, and the dimensions of the test cylinder.
ν = kinematic viscosity of the liquid
s = speed of withdrawal.
n, k' = quantities which are nearly constant but which change slightly with the nature of the liquid.

Figure 2 is a graph of the data in which log t has been plotted against log (νs). It will be noted that the data for the different liquids overlaps; liquids of low viscosity at higher speeds yielded the same results as more viscous ones in which the withdrawal was slower. The slope of the lines is about 0.63, and the value of k' as determined from the intercept is about 0.015.

In order to compare the equation constants of the different liquids, the values of n were computed for each liquid, using the method of least squares. Table 2 presents the results. The coefficient k' was next computed, using the average slope for each liquid and the coordinates of the mean point of each set of observations. The results are shown in table 3.

TABLE 2.—*Summary of values of n*

Liquid	Length of immersion					Average value
	3 cm	5 cm	10 cm	15 cm	25 cm	
Mineral oil 1	0.638	0.650	0.647	0.643	0.640	0.644
Mineral oil 2	.642	.645	.650	.646	.642	.645
Mineral oil 3	.641	.644	.645	.644	.644	.644
Mineral oil 4	.647	.644	.641	.639	.641	.642
Dibutyl phthalate	.624	.623	.619	.617	.622	.621
Aroclor	.633	.630	.632	.630	.630	.631
Peanut oil	.616	.623	.622	.628	.626	.623
Sperm oil	.627	.632	.632	.631	.633	.631
Lard oil	.620	.616	.621	.620	.612	.618

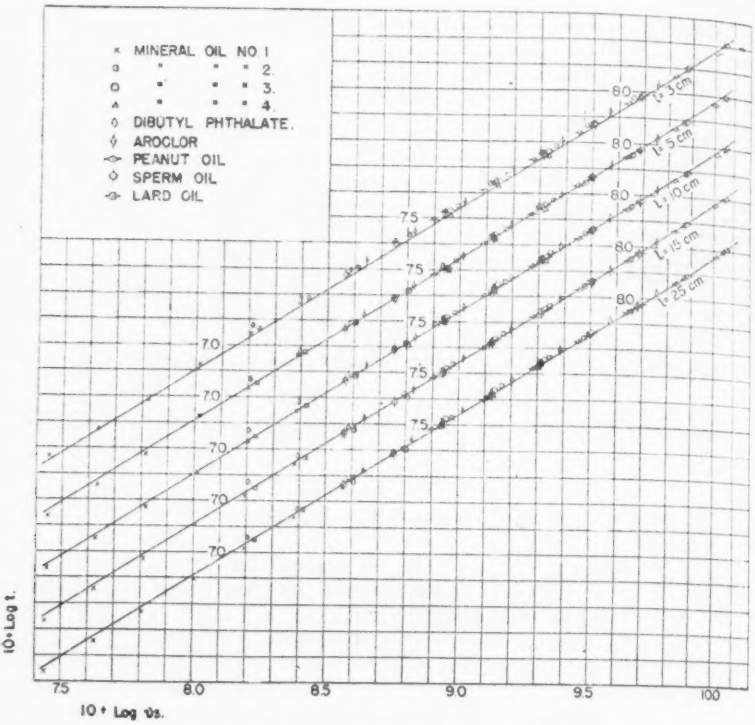

FIGURE 2.—*Graph of observed film thicknesses.*

TABLE 3.—*Summary of values of k'*

Liquid	Length of immersion				
	3 cm	5 cm	10 cm	15 cm	25 cm
Mineral oil 1	0.01585	0.01544	0.01518	0.01520	0.01517
Mineral oil 2	.01589	.01561	.01549	.01546	.01542
Mineral oil 3	.01600	.01552	.01521	.01505	.01497
Mineral oil 4	.01500	.01487	.01485	.01490	.01492
Dibutyl phthalate	.01521	.01499	.01495	.01483	.01467
Aroclor	.01541	.01518	.01502	.01502	.01503
Peanut oil	.01502	.01478	.01470	.01467	.01462
Sperm oil	.01520	.01494	.01484	.01482	.01477
Lard oil	.01497	.01479	.01465	.01463	.01468

The values of k' will be seen to decrease, in general, as the length of immersion increases. This suggests a small correction on the length which is partly due to the capillary elevation of the surface of the liquid where it contacts the test cylinder. This elevation increases the wetted length slightly, and naturally will be of greatest relative importance where the immersion distance is least. Another reason for this correction is that a small amount of liquid adheres to the lower edge of the cylinder in the form of a drop when the film breaks away from the bath. The amount of liquid retained in this fashion is probably quite small, since the thickness of the metal is only 0.013 cm.

This drop should not be confused with that which forms as the oil film on the metal surface drains down and clings to the bottom edge. The latter accumulation is part of the film whose thickness is to be determined, and the weighing must be accomplished before any dripping occurs.

In order to evaluate the correction to be applied, the values of k' were plotted against the reciprocal of the wetted length, as illustrated in figure 3. The points may be fairly well represented by straight lines, which when extrapolated to obtain the zero intercept give the value of the constant for a theoretical infinite wetted length. This intercept will be denoted by k.

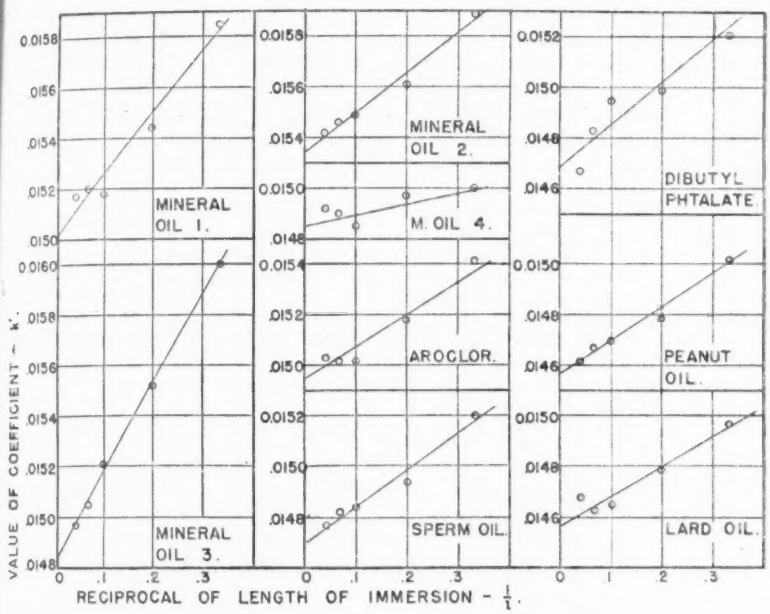

FIGURE 3.—*Variation of coefficient k' with length of immersion.*

The correction term may now be written in the form $(l+b)/l$, where l is the measured immersion length and b is a constant depending upon the kind of liquid used. Thus, by definition,

$$\left(\frac{l+b}{l}\right)k=k'. \tag{2}$$

Also, from the graphs of figure 3,

$$k'=m\frac{1}{l}+k, \tag{3}$$

in which m is the slope of the line. By eliminating k' between these equations and solving for b, it is readily shown that

$$b=\frac{m}{k}. \tag{4}$$

The values of k and b obtained for the liquids tested are shown in table 4.

TABLE 4.—*Summary of equation constants*

Liquid	k	b	n	Liquid	k	b	n
Mineral oil 1	0.01502	0.158	0.644	Aroclor	0.01495	0.083	0.631
Mineral oil 2	.01534	.102	.645	Peanut oil	.01457	.088	.622
Mineral oil 3	.01483	.236	.644	Sperm oil	.01470	.096	.631
Mineral oil 4	.01485	.003	.642	Lard oil	.01457	.078	.618
Dibutyl phthalate	.01469	.109	.621				

The ability of the equation

$$t=k\frac{l+b}{l}(vs)^n \tag{5}$$

to represent the observed data was tested by comparing the observed film thicknesses with those calculated from eq 5. The results of this comparison are presented in table 5. It will be noted that practically all the residuals are within ± 3 percent of the computed values. This is thought to be within the limits of experimental error for the apparatus used.

TABLE 5.—*Comparison of computed and observed film thicknesses*

Length	Approximate speed	Percentage deviation of observed film thickness from that computed from eq. 5								
		Mineral oil 1	Mineral oil 2	Mineral oil 3	Mineral oil 4	Dibutyl phthalate	Aroclor	Peanut oil	Sperm oil	Lard oil
cm	*cm/sec*									
3	0.110	+3.1	+0.7	−0.1	−0.4	+0.9	+0.2	+0.8	+0.1	−0.6
	.170	−0.1	+.2	−.2	.0	−.4	−.3	+.2	+.8	−.3
	.265	−1.5	−.4	+.4	−.5	−1.5	−.4	+.6	+.8	−.2
	.400	−1.3	+.6	+.2	+4.0	−0.6	+.7	+.7	+.4	+.8
	.600	+0.5	+.1	+.2	+3.0	+.1	+.7	+.2	+.1	+.9
	.930	+.3	+.2	−.1	+0.9	+.1	+1.3	−.1	−.4	+1.0
	1.42	−.4	−.5	−1.4	−.2	+1.1	−0.5	−1.8	−.2	−0.7
15	0.110	.0	−.1	−0.9	+.1	+2.4	−.1	−0.7	−.1	−.4
	.170	+.1	−.6	−.6	+.1	+0.2	−.2	−.8	+.6	−.8
	.265	−.3	−.5	+.8	+.7	−1.1	+.1	.0	.0	−.2
	.400	+1.1	+2.0	+1.4	+1.7	−1.6	+.2	+.6	+.3	.0
	.600	+0.1	+.7	0.0	+1.2	−0.7	+.3	+.6	+.4	+.3
	.930	−.1	+.1	+.2	+0.3	+.2	−.1	+.6	+.3	+.3
	1.42	−.3	−.4	−1.1	−1.7	+1.1	−.6	.0	−.2	−.4
25	0.110	+2.1	+.3	−0.7	+0.6	+0.5	+.1	−.4	−.4	+1.5
	.170	0.0	+.1	−.8	−.9	−.3	+.8	−.8	−.1	+0.9
	.265	+.4	+.9	+1.0	+.7	−1.7	+.3	+.2	+.1	+.7
	.400	−.2	−.1	+0.9	+2.1	−1.9	−.1	+.4	+.2	−.1
	.600	−.2	−.2	.0	+1.5	−0.9	+.3	+.7	−.1	+.1
	.930	+.5	−.1	+.3	+0.2	−.1	−.1	−.3	+.4	+.2
	1.42	+.3	−.4	−1.1	−1.0	+.5	.0	+.1	+.2	−.2

When these experimental results are applied to physical apparatus in which the surface in question is not removed from the liquid bath, the equation is simplified because the capillary elevation remains the same at the beginning and end of the motion. Under these conditions the equation

$$t=k(vs)^n \tag{6}$$

will represent the average film thickness as long as the moving surface is kept in uniform motion or at the instant the motion stops.

IV. CONCLUSIONS

This experiment has demonstrated that over the range of viscosities and speeds used, the assumptions upon which Goucher and Ward based their derivation of the equation for the thickness of the film are incorrect, since the exponent of vs is certainly higher than the one-half power. On the other hand, Jefferys' equation is neither confirmed nor disputed, since this experiment is incapable of specifying what film profile was obtained. It should be noted, however, that the mean ordinate of a parabolic section is two-thirds of the maximum ordinate of that section. Therefore Jefferys' solution would be possible if the thickness of the film near the surface of the oil bath remained constant independent of the length withdrawn.

Although the results presented here are obviously sufficiently exact for computing the small correction necessary in calibrating gas-measuring standards, no satisfactory correlation of the equation constants with the other properties of the liquids has been found, and it is hoped that further studies can be conducted which may reveal the factors which govern the formation of the film.

The writer is greatly indebted to the late Edgar Buckingham for many helpful suggestions concerning this problem.

WASHINGTON, June 14, 1940.

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